VOL. 16 No. 8, pp. 213-240 FEBRUARY 1955

Philips Technical Review

DEALING WITH TECHNICAL PROBLEMS
RELATING TO THE PRODUCTS, PROCESSES AND INVESTIGATIONS OF
THE PHILIPS INDUSTRIES

EDITED BY THE RESEARCH LABORATORY OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN, EINDHOVEN, NETHERLANDS

THE THEORY AND CONSTRUCTION OF GERMANIUM DIODES

by J. C. van VESSEM.

621.314.632:537.311.33

The effective use of germanium diodes does not necessarily require a knowledge of the theory underlying the rectification process in these diodes. For the user, the diode characteristic is sufficient as a starting-point. Nevertheless, the editors of this Review feel that many readers will be interested in what happens inside the germanium crystal. Accordingly, current views on the mechanism of crystal rectification and certain details of the design and manufacture of point-contact germanium diodes are discused in the present article as an introduction to the subsequent article on the application of point-contact germanium diodes.

The present insight into the processes of rectification and transistor action in germanium crystals is largely due to Shockley and his associates, whose descriptions of these processes, some scientific and others written in a more popular style, have appeared in various publications [1]).

One of the most important features of these crystals is that conduction takes place in them through the movement of two different types of charge-carrier, known as "free (or excess) electrons" and "holes"; these carriers are mostly generated in pairs (one of each type) and may likewise vanish in pairs by recombination. Rectification takes place under certain conditions as a result of a subtle interplay between charge movements produced by electric fields and diffusion, and the above-mentioned processes of generation and recombination. This will now be explained more fully.

Electrical conduction in germanium

Free electrons and holes in pure germanium

Germanium, like silicon, selenium and tellurium, belongs to a group of semi-conductors owing their conductivity exclusively to electrons, since, as we shall see later, what is known as conduction by "holes" is in fact also a transport of charge by electrons. Semi-conductors in which the charge transport is effected by ions also exist, but belong to another group which will not be discussed here.

In a crystal of silicon or germanium, each atom is situated at the centre of gravity of a tetrahedron formed by the four adjacent atoms to which it is bound. Each bond between two atoms is attributable to an electron-pair of one valence electron from each atom (a so-called covalent, or homopolar, bond). Thus the four valence electrons of each atom are all involved in similar bonds. A two-dimensional representation of such an array will be seen in *fig. 1*.

Thermal vibrations in the crystal lattice may eject an electron from its position. However, such vibrations can only release valence electrons, since the other electrons of the atom are bound too tightly to the nucleus. In fact, the probability that even a valence electron will be so ejected is very small, since it must not only have sufficient energy, but the local situation must be such that an escape-path may be formed. This is equivalent to saying that for release to occur it must be possible for the laws of conservation of both energy and momentum to be satisfied. For the same reason, however, the probability that an electron will drop back to the original site when once released is likewise small; it is then virtually isolated. Nevertheless, such an electron tends to linger in the vicinity of the vacant

[1]) See W. Shockley, Transistor electronics: imperfections, unipolar and analog transistors, Proc. Inst. Rad. Engrs. **40**, 1289 - 1313, 1952. Also W. Shockley, Electrons and holes in semiconductors, D. van Nostrand, New York and London, 1950.

site (or hole), owing to the presence at this site of a non-compensated nuclear charge, which attracts it. Because the two charges attracted to one another are in a dielectric (i.e. germanium, where the dielectric constant $\varepsilon_r = 16$), the attraction is weak; even at room temperature the electron is more or less free to drift through the crystal at random under the influence of thermal agitation.

The holes are also affected by thermal agitation. A hole may easily become occupied by a valence electron from an adjacent bond, leaving another hole at the original site of the electron thus displaced. Again, a valence electron may move into the new hole, and so the process will continue. In effect, then, the original hole roams through the crystal.

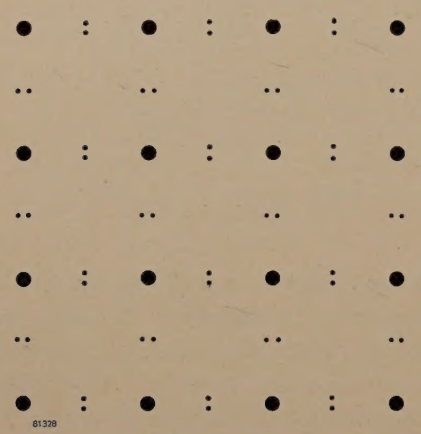


Fig. 1. Two-dimensional representation of the germanium crystal lattice. The large dots represent germanium atoms, and the smaller ones valence electrons paired to form homopolar bonds between each atom and its four immediate neighbours.

The conductivity of pure silicon and germanium

Given an electric field in a piece of pure silicon or germanium, free electrons and holes will both contribute to the flow of current. The contribution of the free electrons requires no explanation; that of the holes arises as follows. The holes tend to become occupied by those valence electrons which, in moving into them, submit to the thrust exerted by the field. Since the electrons move against the field, the holes move with it, i.e. they behave like positively charged particles.

The precise conductivity of a material depends (amongst other things) on the number of free electrons and holes in it. Now, the generation of free electrons and holes is continuous but, at the same time, recombination, that is, the filling of holes by free electrons, is also taking place. In the equilibrium state, the number of charge-carriers generated and the number recombined per unit time and volume are exactly equal. The respective concentrations n (for negative) and p (for positive) of free electrons and holes, identical in pure silicon or germanium, are invariably so small as compared with the concentration of atoms that the rate of generation of charge carriers is not noticeably affected by the number of valence electrons already released; hence the rate of generation may be considered as a constant (C). On the other hand, the number of recombinations is proportional to the concentration of free electrons as well as to the concentration of holes, and may therefore be defined as cnp, c being a constant. Accordingly, the equilibrium values of n and p are governed by the following equations:

$$c\,n\,p = C \quad \ldots\ldots\ldots \quad (1)$$

and

$$n - p = 0\,, \quad \ldots\ldots\ldots \quad (2)$$

giving:

$$n = p = \sqrt{C/c} \quad \ldots\ldots \quad (3)$$

The constants C and c are both functions of the temperature; a rise in temperature will produce sharp increase in C, but only a relatively small increase in c, thus increasing the conductivity. This is a characteristic property of all semi-conductors.

The bond between valence electrons and nuclei is slightly weaker in germanium than in silicon; hence germanium is the better conductor at a given temperature. In diamond, the crystal structure of which resembles that of silicon, the valence electrons are bound so tightly to the nucleus that the number of charge-carriers generated is negligible. Diamond is therefore an insulator.

The conductivity of germanium, though high compared to diamond, is still quite low. At room temperature, pure copper is roughly 10 million times better conducting than pure germanium.

The effect of "impurities"

Germanium is adapted to the purpose of rectification by dissolving small quantities of certain elements ("impurities") in it. For example, arsenic is a suitable impurity. The arsenic atom, which can be substituted for a germanium atom in the germanium lattice, has five valence electrons instead of four. Hence one of these five electrons can find no place in the germanium valence-bond structure and will at first wander more or less at random in the vicinity of the arsenic atom. The latter, having lost one of its electrons, now has a non-compensated nuclear charge. Owing to the effect of the dielectric, the attraction between this positive nuclear charge and the fifth valence electron is rather weak. Even at room temperature, then, thermal vibrations

readily free the surplus electron so that it is in no way distinguishable from others released from valence bonds.

Impurities of the same type as arsenic, that is, those which can supply a free electron, are known as donors. Other donor elements (all pentavalent) are phosphorus, antimony and bismuth.

The addition of a trivalent element, such as boron or indium, creates an entirely different situation. One of the bonds is then deficient of one electron; hence there is a vacant site into which an electron from an adjoining bond can move. The energy level of the electron thus transferred is somewhat higher in the new site than in a normal bond, owing to the fact that here its charge is not compensated by a positive charge in the nucleus, but this extra energy is readily supplied by thermal agitation. A valence electron moving into the vacant site in a boron atom leaves a hole behind. Again by reason of the dielectric, the attraction between the hole and the negative boron ion is weak. Hence the hole easily diffuses away and so prevents the extra electron captured by the boron atom from returning. Eventually, of course, another hole will approach the boron atom, thus enabling the captive electron to escape, but on an average the electron will remain in this energetically less favourable position for some time.

Because they capture electrons, trivalent impurities are described as acceptors. Acceptors, then, promote the generation of excess holes.

Germanium incorporating both donors and acceptors

A type of germanium with which we are very often concerned is that in which both donors and acceptors are present. Contrary to what may be expected, the numbers of free electrons and holes do not both increase, owing to the fact that these different carriers recombine in the manner already described. We shall now go more deeply into this question.

The mechanism of the direct generation and recombination of free electrons and holes as a result of thermal agitation in the crystal, which was tacitly assumed to be the only active mechanism in the case of pure germanium, is likewise active when both donor and acceptor impurities are present. However, other mechanisms of generation and recombination may be present. Now a theorem of statistical mechanics states that, if a phenomenon is promoted simultaneously by different independent mechanisms, the resulting equilibrium concentration will be independent of the number or nature of these mechanisms [2]). (As a possible second mechanism we have, for example, a process of generation in which a valence electron is first captured by a donor which has emitted its own excess electron, and then released, recombination taking place via the same intermediate stage, but in the opposite direction.) The existence of more than one active mechanism will affect the speed with which equilibrium is attained but not the equilibrium itself (catalytic action).

Since the concentrations of the impurities are relatively very low (e.g. 1 impurity centre per 100 million atoms) they do not for practical purposes affect the direct processes of generation and recombination. Hence these direct processes are indeed independent, and the equilibrium concentrations can be computed on the basis of this mechanism alone.

Accordingly, formula (1) is still valid. We can re-write this equation:

$$p\,n = C/c = N_i^2 \quad . \; . \; . \; . \; . \; . \quad (4)$$

where N_i represents the equivalent values of n and p in pure germanium (suffix i for "intrinsic").

Equation (2), on the other hand, takes a different form. At room temperature, almost all the donors have produced electrons, and almost all the acceptors holes. Accordingly, the donors and acceptors (concentrations N_d and N_a respectively) are incorporated in the crystal lattice as fixed positive and negative charges, the combined charge-density of which is $N_d - N_a$. The holes and free electrons (motile charges) give a charge-density $p - n$, and, since the crystal is neutral, we have:

$$p - n = -(N_d - N_a) \quad . \; . \; . \; . \quad (5)$$

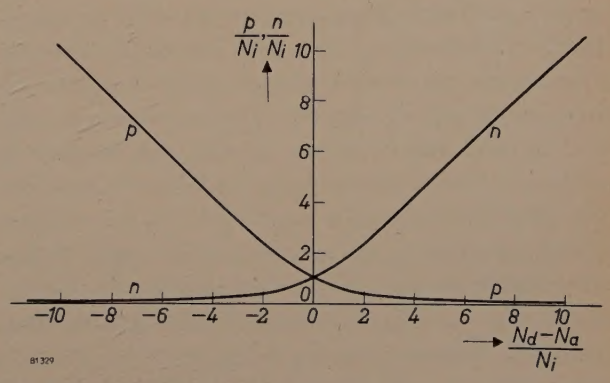


Fig. 2. Equilibrium concentrations of free electrons (n) and holes (p) in a semi-conductor, plotted as a function of the difference in concentration of donors and acceptors ($N_d - N_a$). The concentration (N_i) of free electrons in the pure semi-conductor ($N_d = N_a = 0$) is taken as the unit of concentration for both co-ordinates.

[2]) The proposition is based on the "principle of detailed balancing".

Formulae (4) and (5) establish p and n completely as functions of N_i and $N_d - N_a$. In *fig. 2*, p and n are plotted against the excess of donors $N_d - N_a$. For both co-ordinates, N_i is taken as unity. Germanium with an excess of donors produces a high concentration of free electrons and a low concentration of holes. It conducts primarily by electrons, and is therefore known as n-germanium. On the other hand, germanium with an excess of acceptors produces a high concentration of holes and a low concentration of free electrons; it conducts mainly by holes (which behave like positive charge-carriers) and is therefore known as p-germanium.

The p-n transition zone

Let us now consider the case of a germanium crystal in which the concentrations of donors and acceptors are so distributed as to create a localized region of transition from p-germanium to n-germanium. The associated variation of $N_d - N_a$, i.e. the difference in the concentrations of donors and acceptors, at such a "p-n junction" will be seen in *fig. 3a*. In the following discussion, it is assumed that all the quantities involved depend solely upon the x co-ordinate. Fig. 3*b* shows the distribution of the concentrations of free electrons and holes corresponding to the local values of $N_d - N_a$ given in fig. 2. This curve is not consistent with a state of equilibrium. A concentration gradient of free electrons, and a concentration gradient of holes is set up in the transition zone. These gradients produce diffusion currents of free electrons travelling to the p-region and of holes travelling to the n-region, thus creating a deficit of negative charge in the n-region and an excess of negative charge in the p-region. Accordingly, a region of positive space-charge is formed on the right-hand side of the junction and a region of negative space-charge on the left-hand side, in other words an electric double layer, roughly as shown in fig. 3*c*, is formed. This gives rise to an electric field, which drives the free electrons back to the n-region, and the holes back to the p-region (fig. 3*d*). Equilibrium is reached when the electric field is just strong enough to prevent any further diffusion of charges. The above-mentioned electric double layer sets up the potential difference between the n and p regions, shown in fig. 3*e*.

An expression for this potential difference, which will be found very useful when we discuss the process of rectification, will now be formulated.

The density w_n of the free electron stream in the positive x-direction may be expressed as:

$$w_n = -\mu_n E n - D_n \frac{dn}{dx} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The first term in the right-hand part of this equation represents the contribution of the electric field (E). This contribution is, of course, proportional to the field and to the concentration (n) of the free electrons. The proportionality constant μ_n is known as the mobility of the electrons; the negative sign prefixed to this term is due to the negative electron charge.

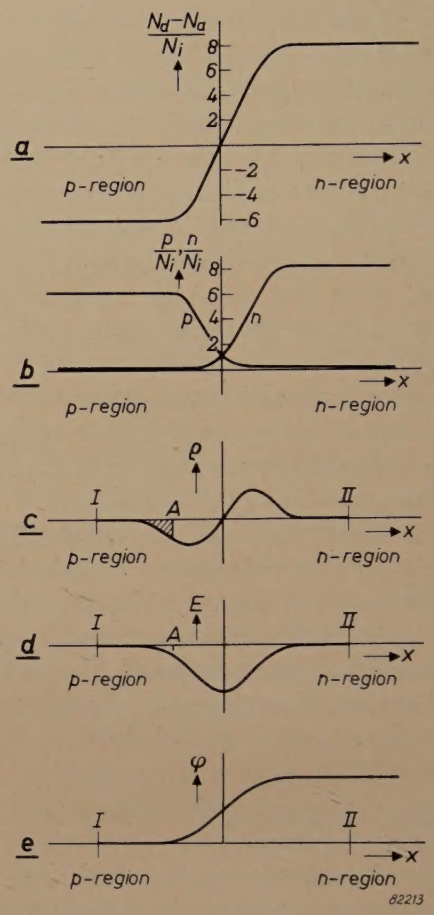


Fig. 3. *a*) Variation of the difference in concentration ($N_d - N_a$) between donors and acceptors at a p-n junction. In the p-region $N_d - N_a < 0$ (excess of acceptors), whereas in the n-region $N_d - N_a > 0$ (excess of donors).
b) Variation of the concentrations of free electrons and holes, n and p respectively, derived from fig. 2, for the variation of $N_d - N_a$ shown in (*a*). In fact, however, diffusion considerably modifies this distribution: the concentrations of both holes and free electrons actually vary more gradually, owing to the diffusion of free electrons to the p-region and holes to the n-region.
c) Space charge density arising from the diffusion of free electrons to the p-region and holes to the n-region. This space charge distribution forms an electric double layer. The hatched area represents the charge which has crossed section A in the p-region.
d) Variation of the electric field E within the electric double layer indicated in (*c*). The hatched area in (*c*) is a measure of the electric field at section A.
e) Potential at a p-n junction. The electrostatic potential relative to an arbitrary zero level is represented by φ.

The second term in the above equation represents the contribution of the diffusion; this is proportional, but opposite, to the concentration gradient dn/dx.

The proportionality constant D_n is the diffusion constant of the free electrons.

In the case here considered (no applied voltage across the crystal), $w_n = 0$ in the stationary state; from (6), then, we have:

$$E = -\frac{D_n}{\mu_n}\frac{1}{n}\frac{\mathrm{d}n}{\mathrm{d}x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If φ be the electric potential, $E = -\mathrm{d}\varphi/\mathrm{d}x$. Considering two sections I and II, one on each side of the transition zone, that is, one in the p, and one in the n germanium (see fig. 3c), and taking n_I and n_{II} as the respective equilibrium concentrations of free electrons at these sections, we find the potential difference φ_0 between the n-zone and the p-zone by integrating (7) from I to II, as follows:

$$\varphi_0 = -\int_I^{II} E\,\mathrm{d}x = \frac{D_n}{\mu_n}\int_I^{II}\frac{1}{n}\,\mathrm{d}n = \frac{D_n}{\mu_n}\ln\frac{n_{II}}{n_I} \quad . \quad (8)$$

Here, then, we have the desired expression for the potential difference.

Similarly, but taking the density of the hole current as a starting point, we deduce that:

$$\varphi_0 = \frac{D_p}{\mu_p}\ln\frac{p_I}{p_{II}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This expression is equivalent to (8) by reason of the fact that, from (4), $p_I n_I = p_{II} n_{II}$ and, in general, $D_n/\mu_n = D_p/\mu_p$. The latter equation is known as the Einstein relation, since it was he that first gave a general proof for it.

Putting

$$\mu_n/D_n = \mu_p/D_p = a,$$

(8) and (9) may be written

$$\frac{n_{II}}{n_I} = \frac{p_I}{p_{II}} = \mathrm{e}^{a\varphi_0} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

To calculate the variation of concentrations n and p in the transition zone as a function of x, and so establish the thickness of this zone, cannot be done in a simple way. With the aid of Poisson's equation, however, it is possible to make a qualitative analysis of the process whereby the diffusion and the electric field reach equilibrium, and so to ascertain that the thickness of the transition zone decreases according as the conductivity increases.

If ϱ be the charge density, ε_0 the dielectric constant of a vacuum, and ε_r the relative dielectric constant of germanium, Poisson's equation in the one-dimensional case here considered is:

$$\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} = -\frac{\varrho}{\varepsilon_0\varepsilon_r}.$$

Since $E = -\mathrm{d}\varphi/\mathrm{d}x$, the above equation may also be written:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\varrho}{\varepsilon_0\varepsilon_r}.$$

Hence:

$$E(x) = \int_{-\infty}^{x}\frac{\varrho}{\varepsilon_0\varepsilon_r}\,\mathrm{d}x. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Accordingly, the hatched area in fig. 3c is a measure of the field strength at section A. If the space charge regions expand, as they will if the diffusion predominates over the electric field, the size of this hatched area will increase, since it represents the charge which has traversed the cross-section A; hence the field strength at A will increase (see (11)). On the other hand, the concentration gradients will decrease, since the variation of the hole concentrations and those of the free electrons, will become more and more gradual. The diffusion will decrease as these gradients decrease. Thus the electric field will gain and the diffusion diminish until a state of equilibrium is established. Given a high conductivity, a small field will be sufficient to maintain a steep concentration gradient in equilibrium. The charge layer will then be quite thin. Similarly, it is seen that if there is a difference in conductivity as between the region on the left and that on the right of the p-n junction, the spread of the space-charge region will be smallest in the zone of high conductivity. In practice, the thickness of the space-charge regions at p-n junctions is of the order of 1 μ.

Rectification at a *p-n* junction

Hypothetical p-n junction in the absence of generation and recombination

It is an apparently incongruous fact that *without the generation and recombination of free electrons and holes, the flow of current in either direction across a p-n junction would be impossible.* This will now be explained more fully, after which it is only a short step to an explanation of the rectification at a p-n junction.

First let us consider the case of a material containing charge carriers of only one type, which are densely concentrated on the left, and sparsely on the right, of a given plane. Here we have simply a good conductor adjoining a poor one. As is well known, when a voltage is applied, a stationary state is established, the condition for continuity of the current flow being satisfied by virtue of the fact that in each conductor the electric field strength is inversely proportional to the conductivity, that is, weaker in the good, than in the poor conductor. Such a state arises from the accumulation of a space charge at the boundary plane between the conductors. This space charge is responsible for the difference in field strength.

However, we are more interested in the case involving two types of charge carrier, i.e. holes and free electrons. Since we exclude the processes of generation and recombination, the electrons and holes must satisfy the continuity condition separately when a current flows, in the stationary state. From the point of view of the holes, the essence of this condition is that the field must be weaker in the

p-germanium than in the n-germanium, whereas the condition for a continuity for the flow of free electron current is precisely the opposite, i.e. that the field be stronger in the p-germanium than in the n-germanium. The only state in which this contradiction does not arise is that in which no current flows and the field strength outside the transition zone is zero. Accordingly, this state must prevail. The whole of the applied potential difference will then be across the p-n junction. As the field strength outside the p-n junction is zero, its gradient dE/dx is also zero and since $\varrho = \varepsilon_0 \varepsilon_r \, dE/dx$ (Poisson) holds good for the space charge density, this signifies that outside the junction the crystal is electrically neutral ($\varrho = 0$).

In the above argument it is assumed by implication that in the stationary state, and at a given distance from the p-n junction, an electric field alone will be responsible for any charge-displacement which may take place, that is, that no concentration gradients, which would give rise to diffusion, are present. This supposition is plausible in itself; hence we do not propose to furnish the proof. Let it suffice to say that a situation in which the concentration gradients do not approach zero as the distance from the p-n junction increases, is found to be incompatible with Poisson's equation, and therefore inconceivable.

The p and n concentrations in the absence of an applied voltage

Equation (7) holds good when no current flows. Accordingly, if the potential difference between n and p germanium be increased by an amount $\Delta\varphi$ through the application of a voltage, integration of formula (7) from section I to section II should produce the result $\varphi_0 + \Delta\varphi$. It can only do so if the equilibrium concentrations of the free electrons and holes change. We shall employ dashed symbols to distinguish the modified concentrations from the original ones.

Integration of equation (7) produces:

$$\varphi_0 + \Delta\varphi = \frac{D_n}{\mu_n} \ln \frac{n_{II}'}{n_I'},$$

which, with the aid of (10), can be put in the form:

$$\frac{n_{II}'}{n_I'} = \frac{n_{II}}{n_I} e^{+a\Delta\varphi} \quad . \; . \; . \; . \; . \; . \; . \quad (12)$$

A similar formula holds good for the modified concentrations of holes:

$$\frac{p_{II}'}{p_I'} = \frac{p_{II}}{p_I} e^{-a\Delta\varphi} \quad . \; . \; . \; . \; . \; . \; . \quad (13)$$

Moreover, it follows from the neutrality condition that the changes in the concentrations of the free electrons and holes must be equal.

In the case of p-germanium, then:

$$n_I' - n_I = p_I' - p_I, \quad . \; . \; . \; . \; . \quad (14)$$

and in that of n-germanium:

$$n_{II}' - n_{II} = p_{II}' - p_{II}. \quad . \; . \; . \quad (15)$$

Equations (12) to (15) determine the four modified equilibrium concentrations. These equations are easily solved. In *fig. 4*, the concentrations as calculated in a given case are plotted as a function of $\Delta\varphi$. It is seen that a given increase in the potential difference between the n and p regions (say, $a\Delta\varphi = +2$) produces only a small drop in concentration. On the other hand, an equivalent decrease in this potential difference ($a\Delta\varphi = -2$) produces a very considerable rise in concentration. This is by no means surprising, because the values of the concentrations have a natural lower limit, that is, they can not fall below the zero level of the so-called minority charge carriers (i.e. the free electrons in the p-region and the holes in the n-region). On the other hand, increases in concentration are not so limited. As

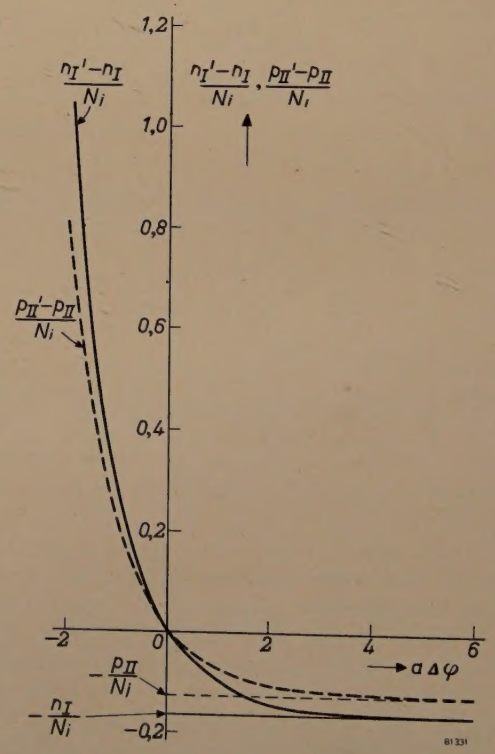


Fig. 4. The variation in concentration of holes and free electrons in the p-region (solid line: $p_I' - p_I = n_I' - n_I$) and in the n-region (dotted line: $p_{II}' - p_{II} = n_{II}' - n_{II}$), respectively, as functions of $\Delta\varphi$, that is, of the change in potential difference between the n and p regions due to an applied voltage. These curves refer to the p-n junction represented in fig. 3. At room temperature $a \approx 40$ volt^{-1}; hence $a\Delta\varphi \approx \pm 40$ when $\Delta\varphi = \pm 1$ Volt. For the ordinate, N_i is again taken as the unit of concentration.

will be explained later, this difference in behaviour arising from a difference in the polarity of $\Delta\varphi$ is responsible for the rectification at a *p-n* junction.

For not too large negative values of $a\Delta\varphi$, the changes in concentration conform to a simple power of e. Eliminating n_{II}' from (12) with the aid of (15), we write:

$$n_I' = n_I\, e^{-a\varphi\Delta}\left(1 + \frac{p_{II}' - p_{II}}{n_{II}}\right).$$

Now as n_{II} is a majority carrier, $n_{II} \gg N_i$. Hence for negative values of $a\Delta\varphi$ which are not so large as to make $(p_{II}'-p_I)/N_i$ very much larger than unity (see fig. 4), $(p_{II}'-p_I)/n_{II}$ may be neglected in comparison to unity. In that case we have $n_I' = n_I\, e^{-\Delta\varphi}$ and hence:

$$n_I' - n_I = p_I' - p_I = n_I(e^{-a\Delta\varphi} - 1) \quad . \quad . \quad . \quad (16a)$$

Similarly, we find that:

$$p_{II}' - p_{II} = n_{II}' - n_{II} = p_{II}(e^{-a\Delta\varphi} - 1) \quad (16b)$$

Physical picture of non-conductance of the crystal

The process leading to the state discussed in the preceding section may be envisaged in the following manner. If a voltage be applied to the germanium then, initially, a current will flow which in the *p*-region will be composed almost entirely of holes, and in the *n*-region almost entirely of free electrons. To avoid the complications associated with the end contacts of the crystal, it is assumed that the applied voltage is so regulated as to maintain a constant potential difference $\varphi_0 + \Delta\varphi$ between two cross-sections *II* and *I*, situated at positions intermediate between the *p-n* junction and the end contacts in the *n* and *p* regions respectively, (*fig.* 5). If $\Delta\varphi$ be negative, a field exists which urges holes in the *p*-germanium towards the junction and those in the *n*-germanium away from it. At the junction itself, the applied field upsets the previous equilibrium between diffusion of holes($p \rightarrow n$) and the reverse flow due to the spontaneous field, so that a nett surplus of holes flows across the junction. In a similar way, a nett surplus of electrons flows in the opposite direction. As already mentioned, however, this flow cannot persist: it appears that the holes entering the junction from the *p*-region and the electrons entering it from the *n*-region attenuate the double-layer at the junction (fig. 3*c*) and so reduce the spontaneous potential difference across the junction until there is no longer any potential drop in the *p* and *n* regions outside (fig. 5*a*). The field outside the junction is therefore zero, for the whole potential drop $(\varphi_0 + \Delta\varphi)$ now occurs across the junction. At the same time another, important effect takes place. The nett surplus of holes flowing across the junction from the *p*-region diffuse into the *n*-region and so increase the concentration of holes there. As this increased concentration penetrates through the *n*-region, however, the concentration gradient which drives it gradually diminishes, until all diffusion ceases (fig. 6*a*). The invading holes, form a space charge in the *n*-region,

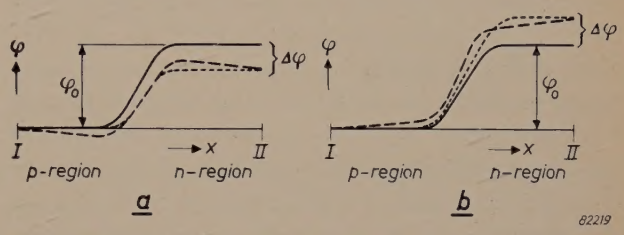


Fig. 5. The potential as a function of position at a *p-n* junction with an applied voltage, in the absence of generation and recombination. In both diagrams, the curve drawn as a solid line refers to the state before the voltage is applied; the potential difference between the *n* and *p* regions is then spontaneous (φ_0). The curves drawn as broken lines apply to the instant when the voltage is applied, and those drawn as dotted lines refer to the subsequent equilibrium state in which no current flows. A potential level of zero is assumed in section *I*. In (*a*) the potential of the *n*-region is reduced, and in (*b*) it is increased, by the applied voltage.

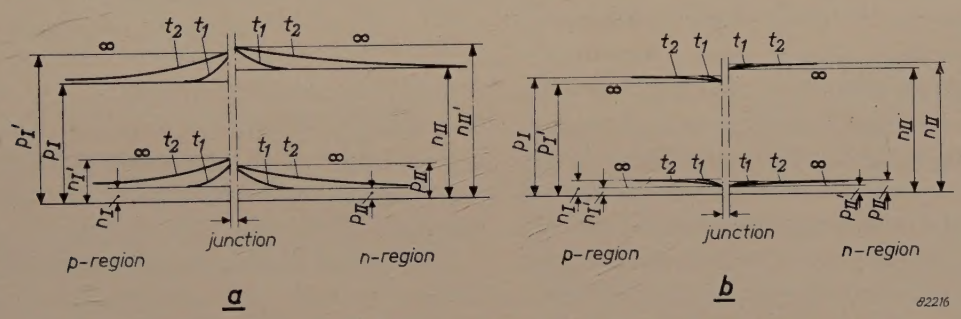


Fig. 6. Three successive stages, viz. at times t_1 and t_2, and at the end of an infinitely long period, during the change in the concentrations of holes and free electrons produced by an applied voltage. Again, it is assumed that generation and recombination do not occur. The changes in concentration develop outwards from the *p-n* junction, thus gradually reducing the concentration gradients to zero. If generation and recombination do occur, a state roughly equivalent to one of the intermediate stages will remain.
a) The applied voltage reduces the potential of the *n*-region relative to that of the *p*-region, and drives holes from the *p*-region to the *n*-region.
b) The same voltage applied in the reverse direction. The decreases in concentration then produced are very much smaller than the increases in case (*a*).

but this is rendered ineffective by an influx of free electrons from the opposite direction; hence the concentrations of the different charge carriers increase simultaneously to the values already calculated (fig. 4). A similar process takes place in the *p*-region, where the free electrons now take the part played by the holes in the *n*-region.

Conversely, by reversing the applied voltage we strengthen the existing electric double layer. The potential jump across the *p-n* junction then increases, again reducing the field outside the transition zone to zero (fig. 5*b*). The shortage of holes in the transition zone resulting from the large-scale migration of holes to the *p*-region now produces in the *n*-region a diffusion current of holes flowing towards the *p-n* junction, thus causing a decrease in the hole-concentration in the *n*-region. This decrease penetrates throughout the *n*-region and so reduces the gradient (fig. 6*b*). Eventually, then, the gradient is eliminated altogether and the diffusion current therefore stops. A simultaneous decrease in the concentration of free electrons prevents the formation of an effective space charge. Again, a similar process takes place in the *p*-region, where the holes and free electrons exchange roles.

An important feature of these processes is that the changes in concentration build up in the crystal from the transition zone.

Conduction as a result of generation and recombination

It is by reason of the generation and recombination of free electrons and holes that in reality a current can flow when a voltage is applied across the crystal. As we have already seen, when $\Delta\varphi$ is negative the concentration of holes and free electrons increase, the origin of this increase being the *p-n* junction (fig. 6*a*). From the start of this increase, the rate of recombination will exceed the rate of generation. This is incompatible with a non-conducting stationary state, since the fact that electrons and holes are eliminated more rapidly than they are generated necessitates a constant influx of these charge carriers, that is, a flow of current.

For example, let us consider what happens in the part of the *n*-region close to the *p-n* junction. Holes diffuse into the *n*-region, creating an enhanced hole-concentration there. As this enhanced concentration penetrates deeper into the *n*-region, so the number of holes eliminated per second by recombination increases, whereas the propagating concentration gradient, and therefore the supply of holes, decreases.

This process leads to a state in which the relatively high concentration extends so far into the *n*-region that the influx and elimination of holes and free electrons are precisely in equilibrium. The necessary supply of free electrons is maintained by virtue of the fact that the electric field outside the *p-n* transition zone does not now disappear completely, contrary to the case when generation and recombination were supposed not to occur. Some of these electrons recombine with holes in the *n*-region and others diffuse into the *p*-region, where they recombine with holes newly introduced by the electric field. The holes so introduced which evade recombination, pass the *p-n* junction and so maintain the diffusion current of holes in the *n*-region.

Similarly, a positive $\Delta\varphi$ produces a stationary state in which regions of relatively low concentration extend from the *p-n* junction into the *p* and *n* regions in this case, the rate of generation in these regions exceeds the rate of recombination. This state corresponds roughly to one of the intermediate stages shown in fig. 6*b*.

In a stationary state of this kind, a current must flow to provide an outlet for the excess free electrons and holes generated.

Magnitude of the current; rectification

Whether $\Delta\varphi$ be positive or negative, minority charge carriers are propagated by diffusion, and majority charge carriers by the electric field. Of course, the electric field also affects the minority carriers, but their concentration is so much lower than that of the majority carriers that an electric field producing an appreciable current of majority carriers will produce virtually no current of minority carriers. For the latter, then, diffusion is the only effective means of propagation. For this reason, it is simpler to consider only the minority charge carriers and, in fact, this enables conclusions to be reached without considering the more complex behaviour of the majority carriers.

The current in each section is the sum of the free electron and the hole components; hence this is true, for example, at the section of the *p*-region adjoining the transition zone. Now, the transition zone itself is invariably so narrow that the number of charge carriers generated and recombined in it is negligible. Accordingly, the hole current (produced by the field) in the boundary plane at the *p*-side is equal to the hole current (produced by diffusion) at the *n*-side of the junction. Hence the total current (= hole current + electron current) may be expressed as the sum of the diffusion currents of the minority charge carriers (electrons in *p*-region and holes in *n*-region) at the two boundary planes of the transition zone.

A diffusion current is proportional to the concentration gradient. If deviation from the equilibrium concentration is large, the rates of elimination and generation of the charge carriers will also be large and hence a steep concentration gradient will be set up. The diffusion current will then be correspondingly strong. Now, the curves shown in fig. 4 are still valid, to a first approximation, for the changes in concentration in the boundary planes of the transition zone. Accordingly, the diffusion currents occurring in these two boundary planes will be appreciably stronger at a given negative value of $\Delta\varphi$ than at the equivalent positive value, i.e. rectification takes place. In the former case, which is the "forward direction" the applied voltage drives holes from the p-region and free electrons from the n-region to the p-n junction (see fig. 5a). When the applied voltage is reversed ($\Delta\varphi$ positive) holes are driven from the n-region and electrons from the p-region; conduction is then much smaller, and in the "reverse direction".

A quantitative analysis of the process can also be made without undue difficulty. The effect of the electric field on the minority charge carriers may be neglected. Hence from the point of view of the free electrons in the p-region, equation (6) is reduced to:

$$w_n = -D_n \frac{dn}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Given two sections, a distance dx apart, in the p-region (*fig.* 7), we find that the number of free electrons entering this element through the left-hand boundary plane exceeds the number leaving it through the right hand boundary plane, per second and per unit area, by an amount $-(dw_n/dx)dx$, which, from (17), is equal to $D_n(d^2n/dx^2)dx$. Hence the excess influx per unit volume per second is $D_n d^2n/dx^2$.

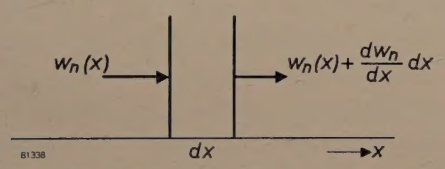


Fig. 7. Diagram illustrating the derivation of the expression for the concentration gradient of minority charge carriers.

In equilibrium, this difference is equal to the numerical surplus of free electrons eliminated (by recombination), over free electrons added (by generation), per second and per unit volume. For the present, let us consider only the direct processes of generation and recombination; the number of carriers generated is then constant, viz C (see earlier), and the number of recombinations is $cnp = c\,(n_I + \Delta n)\,.\,(p_I + \Delta p)$, where Δn and Δp represent the deviations from the respective equilibrium concentrations n_I and p_I in the p-region. Bearing in mind that n_I (minority charge carriers) is very low, and that $cn_Ip_I = C$ (see (1)), we find that the number of recombinations exceeds the number of carriers generated by $cp_I\Delta n$. Other mechanisms of generation and recombination likewise produce a surplus of recombinations, proportional to Δn; in general, then, we may define this surplus as $b\Delta n$, b being a constant. Since, furthermore, $d^2n/dx^2 = d^2\Delta n/dx^2$, we have:

$$D_n \frac{d^2\Delta n}{dx^2} = b\Delta n\,.$$

The boundary conditions of this differential equation are: $\Delta n = 0$ for $x = -\infty$, and (see (16a)) $\Delta n = n_I\,(e^{-a\Delta\varphi} - 1)$ for $x = 0$ (assuming that the p-n junction is located at $x = 0$). The solution is:

$$\Delta n = n_I\,(e^{-a\Delta\varphi} - 1)\,e^{x/L_n}\,,$$

where $L_n = \sqrt{D_n/b}$ is known as the diffusion length for free electrons.
For $x = 0$, we have:

$$\left(\frac{dn}{dx}\right)_{x=0} = \left(\frac{d\Delta n}{dn}\right)_{x=0} = \frac{1}{L_n} n_I\,(e^{-a\Delta\varphi} - 1).$$

Hence the diffusion current of free electrons at the p-n junction is (see (17)):

$$w_n = -n_I \frac{D_n}{L_n}\,(e^{-a\Delta\varphi} - 1).$$

Similarly, we find that the diffusion current of holes at the p-n junction, is:

$$w_p = p_{II} \frac{D_p}{L_p}\,(e^{-a\Delta\varphi} - 1).$$

Accordingly (if $-e$ is the charge on the electron), the total current (i) is:

$$i = ew_p - ew_n = \left(\frac{D_p}{L_p} p_{II} + \frac{D_n}{L_n} n_I\right) e\,(e^{-a\Delta\varphi} - 1). \quad . \quad (18)$$

When $\Delta\varphi = +\infty$, the current i approaches the saturation value $-i_s$ of the leakage current (the minus sign is added to denote current in the reverse direction i.e. in the negative x-direction):

$$-i_s = -\left(\frac{D_p}{L_p} p_{II} + \frac{D_n}{L_n} n_I\right) e,$$

which enables us to write formula (18):

$$i = i_s\,(e^{-a\Delta\varphi} - 1).$$

The formation of *p-n* junctions

Such p-n junctions as we are now considering may occur in several ways. They sometimes occur as a result of a non-uniform distribution of impurities during solidification of a melt of germanium. Again, they may be formed deliberately in many ways, e.g. by adding the desired impurities suddenly to the molten germanium during the process of crystallization.

For some purposes, crystal diodes are made by establishing a p-n juncton, such as discussed above, in a single crystal of germanium. A more common form of the crystal diode, however, is the point con-

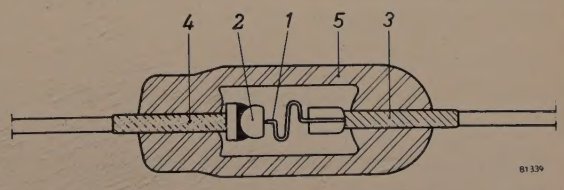


Fig. 8. Construction of a point-contact germanium diode of the latest type. The pointed contact spring *1* presses against the germanium crystal *2*. The contact spring and the crystal are secured to supporting pins *3* and *4*, sealed into a glass bulb *5* as protection against the atmosphere.

tact diode (*fig. 8*). It is now generally accepted that rectification in a modern point-contact diode (fig. 8) is also attributable to a *p-n* junction [3]). After the application of the point contact to the germanium crystal, several current pulses of high intensity are passed through the diode (a process known as "forming" the contact). This enables impurities to diffuse from the crystal surface or out of the contact spring into the crystal and so form a *p-n* junction around the contact point. One may also picture the process as an effect of the current pulses on the local distribution of donors and acceptors near the point, with the formation of a *p-n* junction.

Even without the forming process, any contact between a metal and a semi-conductor will act as rectifier. No entirely adequate explanation of the mechanism responsible for this rectification has yet been given, and we shall not pursue the matter further here, since it plays only a minor role in the point-contact diode: once the contact has been "formed", rectification at the *p-n* junction so established will dominate over any other mechanisms. *Fig. 9* shows the rectification characteristics of a point-contact germanium diode before and after "forming".

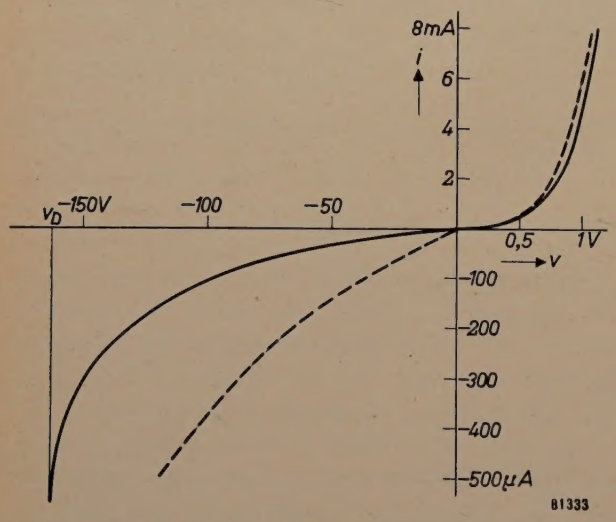


Fig. 9. The rectification characteristic (current i as a function of the applied voltage v) of a point-contact germanium diode (type OA 71). v_D is the breakdown voltage, at which $d_v/d_i = 0$. The dotted curve is the characteristic of the same diode before the forming process. Note the difference in the scales used for the voltage in the forward and reverse directions and also for the forward and leakage currents.

As mentioned above, the point-contact is not the only form of *p-n* junction with rectifying properties. However, the capacitative effect of such a contact is small (stray capacitance of the order of one or two pico-farads); hence point-contact diodes offer certain advantages for high-frequency operation. On the other hand, diodes with a *p-n* junction of relatively large area (and consequently higher stray capacitance), are useful for other purposes, e.g. power operation at heavier currents.

The rectification characteristic

As will be seen from fig. 9, the leakage current increases with the negative bias until, at point v_D, the dynamic resistance dv/di of the diode is zero. The voltage to produce this effect is known as the breakdown voltage of the diode, since, unless the current be limited by a suitable ballast resistor, breakdown will occur when the voltage accros the diode reaches the value corresponding to v_D. The breakdown voltage varies between different types of diode; for example, $v_D \geqq 30$ V for the OA 60, whereas $v_D \geqq 120$ V for the OA 55. Germanium diodes with breakdown voltages higher than 300 V are occasionally produced, but so far no one has succeeded in producing diodes with this value in a normal production run.

The primary cause of breakdown is heat generated by the current flowing in the crystal. This liberates free electrons and holes, which reduce the internal resistance of the crystal and so increase the leakage current, thus generating more heat; hence still more free electrons are released and so the process continues until the internal resistance of the crystal is virtually zero. However, if the same voltage be applied in short pulses instead of continuously, this "avalanche" will not have time to develop. According to the above theory, then, the breakdown voltage v_D is higher under these conditions.

The breakdown voltage of Philips diodes are measured statically, that is, under the most unfavourable conditions. In practice, a certain safety margin must be preserved; this is accomplished by imposing two restrictions on the reverse voltage. These restrictions are that the reverse *peak* voltage must not exceed a certain value and that the *average* reverse voltage must not exceed another specified value.

In the forward direction, the increase in current with voltage is fairly gradual within the range up to about 0.5 V; beyond this range it is rapid and nearly linear (fig. 9). The current in the forward direction at 1 volt is usually given as the characteristic quantity for a diode; it represents the average increase in current per volt within the range between 0 and + 1 volt. At + 1 volt, of course, the actual slope of the characteristic in mA/volt is considerably greater than this average value.

[3]) See M. C. Waltz, Proc. Inst. Rad. Engrs. **40**, 1483 - 1487, 1952, and Makoto Kikuchi and Tomio Onishi, J. appl. Phys. **24**, 162-166, 1953.

The manufacture of point-contact germanium diodes.

The basic material is spectrochemically pure germanium dioxide (GeO_2), obtained as a by-product of certain zinc ores. It is reduced in a hydrogen atmosphere to pure germanium, which, if necessary,

Fig. 10. A boat (of graphite) containing pure germanium dioxide powder. In front of the boat is a sample of the black, metallic germanium powder obtained by reducing the oxide. A rod of germanium metal, which is a single crystal, and a germanium diode are shown in the foreground.

can be further refined by fractional crystallization (*fig. 10*). At this stage, a pre-determined quantity of a suitable impurity may be added to, and melted with, the germanium. The next step is to divide the germanium into small pieces and solder them to nickel supporting-pins. Special measures are taken to prevent rectification at the contacts formed during this process. The top face of the crystal is then ground smooth; since this grinding seriously affects the crystal orientation of the top layer, the latter is removed by etching with hydrofluoric acid. The supporting pin carrying the crystal is then sealed into a glass bulb fitted with lead-in caps of fernico, and a similar pin carrying a thin spring of tungsten wire is inserted in the bulb from the opposite end so that the spring contact presses firmly against the crystal. The second pin is then also sealed into the bulb (see *fig. 11*). Either a piece of polycrystalline germanium, or a single crystal may be employed, according to the particular diode properties required. A considerable improvement of the rectification characteristic is effected by passing several strong current-pulses through the germanium ("forming", see above).

Fig. 11. The components of a point-contact germanium diode shown full size. Note the support-shanks, one of which carries a fine contact-spring. Between these shanks lie the glass bulb and the germanium crystal. An assembled diode is seen at the top of the photograph.

The process of soldering the supporting pins in the fernico lead-in caps of the bulb creates a special problem, owing to the fact that the etched germanium surface is readily contaminated by the vapour formed during this process. Such contamination would shorten the life of the diode. For this reason, a protective layer of plastic lacquer, easily pierced by the contact spring, is applied to the germanium surface immediately after the etching process. This layer satisfactorily precludes the above-mentioned effect without detracting from the quality of the diode.

However, in a new type of germanium diode recently introduced, the metal electrode-holders are sealed direct to the glass (fig. 8). The advantage of this method is that it avoids soldering, and so ensures an exceptionally high degree of stability. On the other hand, for technical reasons, the lead-in pins employed in this process must be thinner than those of the glass-fernico diodes already described; this decrease in pin-thickness slightly reduces the heat-dissipation from the crystal and so necessitates a slight lowering of the maximum limits for current and voltage.

In fact, the maximum permissible peak and average values of the reverse voltage for this new type of diode are limited to the fixed values 75% and 50%, respectively, of the breakdown voltage as statically measured.

Behaviour of germanium diodes at high frequencies

Germanium diodes are characterised by what is known as the "hole-storage" effect. We have already seen that in a germanium diode operated in the forward direction, a relatively high concentration of charge carriers occurs in the vicinity of the *p-n* junction. If the voltage applied to the diode be reversed (reverse direction), the leakage current so produced will at first greatly exceed the value indicated by the characteristic, owing to the fact that this relatively high concentration must be reduced to the lower concentration consistent with the normal leakage current (see *fig. 12*).

It can be deduced from fig. 12*b* that the average leakage current in the negative period increases with

the frequency of the a.c. voltage. In a circuit, then, any increase in this frequency will reduce the detection efficiency and the equivalent attenuation resistance [4]). This explains the unsatisfactory results obtained when a standard diode (type OA 50, 51, 53, 55 or 61) is employed, for example, as a video detector. In fact, a special diode (OA 60, and OA 70 in the new series) has been developed for such purposes. When so employed, this diode exhibits

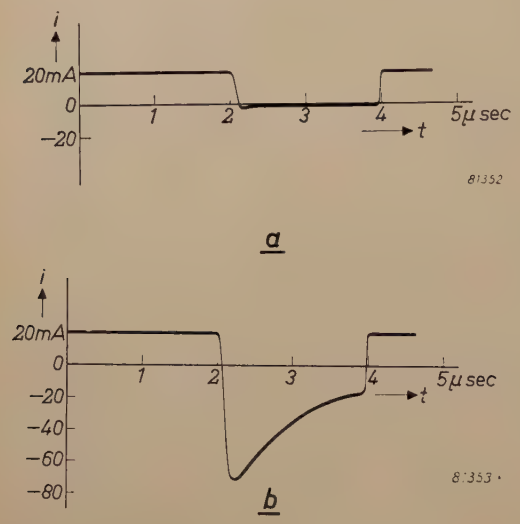


Fig. 12. "Hole storage" effect in two types of point-contact germanium diodes. The curves are taken from oscillograms. In both cases the forward current is 20 mA and the reverse voltage 20 V.
a) Diode showing virtually no hole storage effect.
b) Diode showing considerable hole storage. The leakage current fails to attain its static value even 2 μsec after the application of the reverse voltage. If the period of the voltage pulse in the reverse direction be short, the average value of the leakage current during this period will be high.

dynamic properties considerably better than those of the other, statically superior, diodes.

Difficulties from "hole storage" may also occur in the circuits of calculating machines, where it is important to ensure that only pulses of the required square shape are admitted.

[4]) See the following article on p. 225 of this issue: J. Jager, The application of germanium point-contact diodes.

Behaviour at high temperatures

As the temperature rises, more and more electrons are released from the normal bonds. These electrons, and the holes generated with them, increase the conductivity and so reduce the internal resistance of the diodes.

At temperatures in the region of 65-75 °C, the number of charge-carriers thus generated so far exceeds the number of those introduced artificially, as to virtually suppress the differences between standard diodes such as the OA 50, 51, 55 and 56. It is then necessary, of course, to lower the maximum limit for voltages in the reverse direction as compared with those valid at room temperature (that is, up to 25 °C). The maximum voltage ratings of diodes of the new series, i.e. OA 70, OA 71, and so on, are valid for an ambient temperature up to 60 °C; hence it will be necessary to reduce these ratings only if the ambient temperature exceeds 60 °C.

In general, the ambient temperature of the germanium should be kept as low as possible, and operation at temperatures above 60 °C is to be avoided, since rectification, although it does not cease entirely at such temperatures, cannot then be guaranteed.

Summary. This article discusses at some length the mechanism of rectification in germanium diodes. Pure germanium conducts by electrons and "holes", the latter behaving like positively charged particles. It is possible to change the concentrations of these different charge carriers appreciably by introducing certain foreign elements. The addition of pentavalent elements (donors) increases the number of free electrons and reduces the number of holes, thus producing what is known as *n*-germanium (conduction by negative particles). Conversely, the addition of trivalent elements (acceptors) increases the number of holes and reduces the number of free electrons. The material thus produced is known as *p*-germanium (conduction by positive particles). Given both a *p*-region and an adjoining *n*-region in a single germanium crystal, rectification will take place when a current flows through the crystal across this junction. The explanation of this effect is rather complex; it depends on a subtle interplay between the generation and recombination of electrons and holes and their movements as a result of diffusion and electric fields. It is nowadays generally accepted that rectification in point-contact diodes is also attributable to a *p-n* junction. The probable mechanism of formation of such a junction in a diode of this type is briefly outlined. Particulars are also given of the manufacture of point-contact diodes, their rectification characteristics, and their high-frequency and high-temperature performance.

THE APPLICATION OF POINT-CONTACT GERMANIUM DIODES

by J. JAGER.

621.314.632

Now that germanium diodes are becoming generally available, there is a marked tendency to substitute these small, convenient components for vacuum diodes wherever possible. While it is true that their special properties enable germanium diodes, and point-contact germanium diodes in particular, to be used advantageously for the rectification of relatively low voltages and currents, the vacuum diode is often retained, even in cases where a superficial examination suggests the use of a germanium diode. The purpose of the present article is to give an idea of the relative advantages and disadvantages of germanium and vacuum diodes.

Germanium and vacuum diodes

As compared with the vacuum diode, the germanium diode offers a number of conspicuous advantages, viz:

1) It contains no filament. This advantage is particularly valuable in apparatus where there is no other reason to employ heater power, or where a filament would necessitate the use of long supply leads. Also, of course, it eliminates the problem of the filament as a possible source of hum, as may occur in a vacuum diode when the impedance between the cathode and earth is high.

2) Germanium diodes can be incorporated direct in the wiring merely by soldering the two connecting wires to the appropriate points; only a few types of vacuum tube can be connected in this manner.

3) Germanium diodes are very small and light (weight about 1.1 grams) (*fig. 1*).

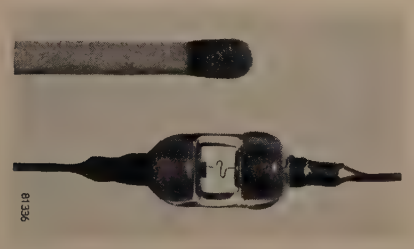


Fig. 1. The small size of point-contact germanium diodes can be judged by comparison with the match head in this photograph. Only two connections are necessary since there is no filament. The diode is mounted without a valve holder.

Features 2) and 3) show to the best advantage in circumstances where the diode is to be accommodated with other components in a relatively small space (e.g. in a coil can).

Apart from these three general advantages, which are direct results of the difference in design of germanium and vacuum diodes [1]), some of the electrical properties of the germanium diode are also superior, viz.:

4) Low shunt capacitance, i.e. about 1 pF, an outstanding feature of point-contact germanium diodes, which may be vitally important at high frequencies.

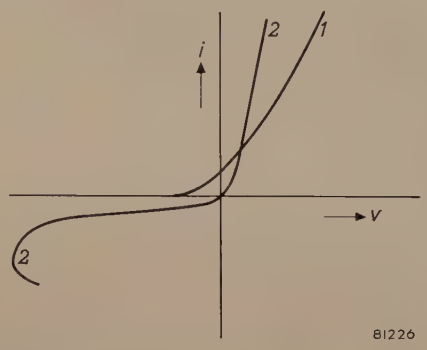


Fig. 2. Characteristics of a vacuum diode (*1*) and a germanium diode (*2*). A vacuum diode in a closed circuit is conductive in the forward direction when no external voltage operates in the circuit, and will even remain conductive in the presence of a small negative voltage (starting-current region). However, it carries no leakage current (current in the reverse direction). On the other hand, a germanium diode has a lower forward resistance and no starting-current region, but does exhibit a leakage current. Also, the differential resistance (dv/di) is zero at a certain negative voltage (vertical tangent to curve).

5) The internal resistance of a germanium diode operated in the forward direction is lower than that of a vacuum diode, even when the latter is specially designed to operate with a low load-resistance.

6) The germanium diode has no starting-current region (*fig. 2*), unlike the vacuum diode, and therefore requires no compensation for starting current in measuring-circuits.

The above summary is impressive and, in fact, these advantages will often turn the scale in favour of the germanium diode. However, this diode has one or two other features which compare unfavourably with those of its vacuum equivalent. They may be defined in the following manner:

a) Whereas a vacuum diode is not conductive in the reverse direction, the germanium diode carries an

[1]) J. C. van Vessum, The theory and construction of germanium diodes, p. 213 of this issue.

appreciable leakage current, particularly at relatively high voltages.

b) A vacuum diode, suitably designed, is able to withstand the application of a high negative voltage between anode and cathode, whereas the shape of the current-voltage characteristic ($i = f(v)$) of the

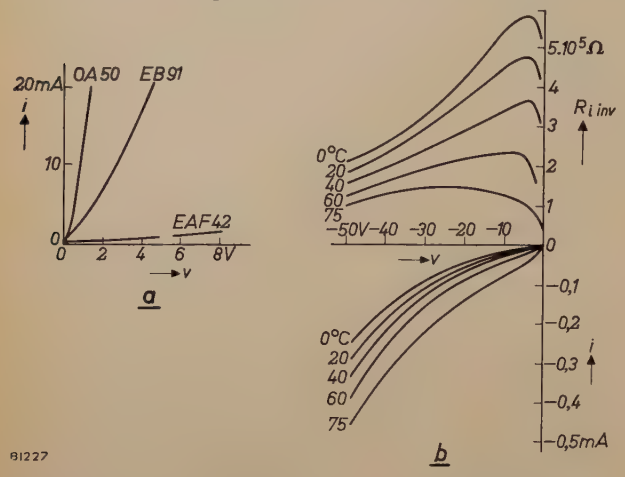


Fig. 3. *a*) Forward characteristics of a general-purpose germanium diode (type OA 50) and of two vacuum diodes, viz one half of an EB 91 double diode, designed to operate with a low load-resistance, and the diode section of a diode-pentode EAF 42, designed to operate with a high load-resistance.
b) The leakage current (i) of a germanium diode type OA 50 versus the applied voltage (v) at different ambient temperatures (bottom part of the diagram). Compare this with (*a*), but note the difference in the scales used in the two diagrams.
The top part of diagram (*b*) shows the ratio $R_{i\,inv} = v/i$, i.e. the leakage resistance, plotted as a function of voltage v.

germanium diode is such that, at a certain voltage, the differential resistance, that is, dv/di, is zero (fig. 2). In those germanium diodes which are most efficient in this respect, zero differential-resistance occurs at about −300 V.

c) The characteristic of a germanium diode depends, to a considerable extent in the forward direction but especially in the reverse direction, on the temperature. The characteristic is also dependent on the rate of change of voltage. This effect becomes important at high frequencies.

All the examples given in this article refer specifically to point-contact germanium diodes, although in referring to them we shall omit the words "point contact" for the sake of brevity.

Fig. 3a shows the forward characteristics of a germanium diode for general service, a vacuum diode designed to operate with a low load-resistance (e.g. 3 kΩ, as employed in the video detectors of television receivers), and a valve of the type used in ordinary radio receivers, where the load-resistance is usually much higher (i.e. about 0.5 MΩ).

The conductivity of the germanium diode in the reverse direction, unlike the two vacuum diodes, is considerable. Fig. 3*b* (bottom half) shows the reverse current of a germanium diode plotted against the voltage, for various ambient temperatures. The upper half of fig. 3*b* shows the corresponding inverse resistance (i.e. the resistance in the reverse direction).

Diodes are extensively used for the detection of amplitude-modulated signals. The differences between vacuum diodes and germanium diodes will now be discussed by a consideration of their applications. One or two practical examples of diodes designed for special purposes will also be discussed.

The performance of vacuum diodes and germanium diodes in detector circuits

The quality of a detector circuit is governed primarily by two quantities, i.e. the detection efficiency and the equivalent attenuation resistance. These quantities will now be discussed more fully, to ascertain how they are affected by the characteristics of the particular diode employed. The results so obtained may help us to decide in a given case whether a germanium diode should be employed, and, if so, which type is most suitable.

Detection efficiency

Fig. 4a shows a circuit of a type frequently employed in detectors. Here, the diode load comprises a resistance R and a capacitance C in parallel.

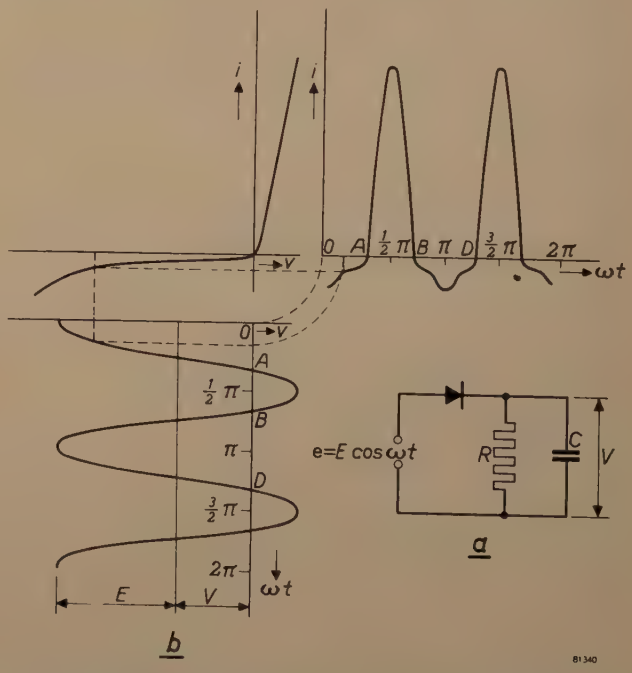


Fig. 4. *a*) Simple circuit for the detection of amplitude-modulated signals.
b) The current in a germanium diode operating in the circuit shown in (*a*), plotted as a function of the time (top right-hand side), as deduced from the signal voltage varying harmonically with time, $e = E \cos \omega t$ (bottom left), and the characteristic of the diode (top left). A leakage current flows in the diode in the interval BD. The D.C. voltage (V) across capacitor C adjusts itself until the ingoing and outgoing charges during a period are exactly equal. The charge-balance so established depends considerably on the discharge current through load-resistance R.

The signal voltage $e = E \cos \omega t$ is supplied by a generator, the internal resistance of which, for simplicity, is assumed to be zero. In reality, E varies (modulation); however, this variation is immaterial to the present discussion, and we may therefore consider E as a constant. Moreover, we shall assume that the time constant (RC) of the load is large compared with the period of the signal voltage; since the ripple on the capacitor voltage will then be small, we may also suppose this voltage (V), to be constant. Accordingly, the voltage across the diode, varying with time, is given by $e - V$. Fig. 4*b* shows the current in a diode, derived as usual from the current-voltage characteristic, for a given arbitrary value of V. As will be seen from this diagram, the charging of the capacitor takes place during a time interval represented by AB. The capacitor discharges a constant current of magnitude V/R through the load resistance; however, part of its charge is also extracted, during another interval BD, through the germanium diode. Of course, the voltage V stabilizes at such a value that the total charge entering the capacitor in one period is equal to that leaving it (charge-balance). Any increase in the leakage through the diode necessitates an increase in the charging-interval AB, which drives the diode further into the region of positive current and so reduces the D.C. voltage V produced across the capacitor. The maximum value which the voltage V can attain is the peak-value E of the applied A.C. voltage; this value would be reached if both the diode inverse resistance and the load resistance were infinitely high. The ratio V/E is commonly known as the detection efficiency, η_{det}. In the case of a germanium diode with an idealized characteristic, that is, two straight lines joining at the origin (*fig. 5a*), the detection efficiency is readily calculated by equating the ingoing and outgoing charges of the capacitor during one period. It is simpler to use the reciprocal resistances (conductances) in the calculation, instead of the resistances themselves; G then represents the conductance of the load resistance, and G_i and $G_{i\,\text{inv}}$ the conductances of the diode in the forward and reverse directions respectively. The calculation is straightforward and is not given here. It proves that η_{det} is a function of $(G + G_{i\,\text{inv}})/(G_i - G_{i\,\text{inv}})$. Since $G_{i\,\text{inv}}$ is invariably $\ll G_i$, $G_{i\,\text{inv}}$ may be neglected in the denominator. The calculation, the result of which will be seen in fig. 5*b* produces a qualitatively correct interpretation of the effect of the various associated quantities on the detection efficiency. (The straight-line approximation to the diode characteristic is too rough for use in practical calculations.) If G be high (that is, R low) in relation to the leakage $G_{i\,\text{inv}}$, the effect of leakage will be negligible. The detection efficiency increases as G decreases, but at the same time the detrimental effect of leakage becomes more and more significant.

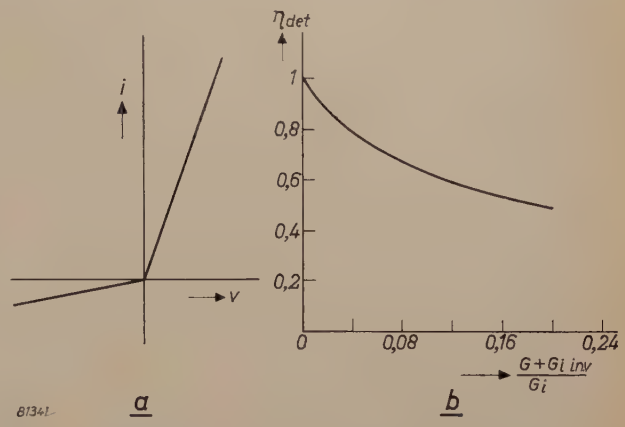


Fig. 5. *a*) Idealized characteristic of a germanium diode, that is, two straight lines meeting at the origin.
b) The detection efficiency η_{det} as calculated for a circuit such as that in fig. 4*a* containing a diode with an idealized characteristic as shown in fig. 5*a*. It is seen that in this case η_{det} is governed solely by the quantity plotted on the abscissa, that is, $(G + G_{i\,\text{inv}})/G_i$, where $G = 1/R$, $G_{i\,\text{inv}} = 1/R_{i\,\text{inv}}$ and $G_i = 1/R_i$ (R being the load-resistance (see fig. 4*a*), $R_{i\,\text{inv}}$ the leakage-resistance of the diode and R_i its forward resistance).

As regards the efficiency, then, a germanium diode cannot possibly compete with any vacuum diode, since in the latter, where $G_{i\,\text{inv}} = 0$, η_{det} approaches unity when G approaches zero (see fig. 5*b*), whereas a germanium diode, with $G_{i\,\text{inv}} \neq 0$, cannot approach this level of efficiency.

Practical tests confirm this theory. Let us consider *fig. 6a* showing the D.C. voltage V, produced across the capacitor, versus the peak value (E) of the signal voltage for the diodes whose characteristics are shown in fig. 3. The curves shown in fig. 6*a* refer to

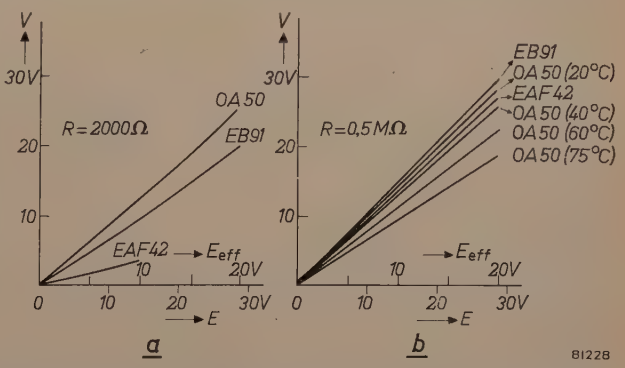


Fig. 6. *a*) The D.C. voltage V produced across the capacitor of a detector circuit as shown in fig. 4*a*, plotted against the peak value E of the applied signal voltage (the r.m.s. value E_{eff} of this voltage has also been plotted on the abscissa of the diagram). In the case considered here, the load-resistance is relatively low, i.e. 2 kΩ. These curves apply to the particular diodes specified in the diagram; the associated characteristics are shown in fig. 3.
b) As (*a*), but with a considerably higher load-resistance, i.e. 0.5 MΩ. In this case, the curve referring to the germanium diode (OA 50) is very dependent on the ambient temperature.

a low load-resistance, i.e. 2 kΩ. Their slight curvature arises from a deviation of the characteristics from the idealized case (straight lines meeting at the origin); G_i and $G_{i\,\mathrm{inv}}$ are not constant, but depend upon the voltage across the diode. Owing to this curvature, the detection efficiency V/E increases with the signal voltage. It will be seen that by virtue of the low load-resistance employed, the favourable forward characteristic of the germanium diode (high G_i) is reflected in a detection efficiency superior to those of the vacuum diodes.

Here, then, the leakage of the germanium diode does not impair its efficiency, as may be deduced from the fact that the curve appropriate to this diode is independent of the ambient temperature. Although a rise in temperature increases the leakage considerably, it has no appreciable effect on the forward resistance. As follows from theory outlined above, the rate of increase of the detection efficiency with the load resistance is higher in vacuum diodes than in germanium diodes. Curves plotted at a very much higher load resistance, i.e. 0.5 MΩ, are shown in fig. 6*b*. The leakage in the germanium diode then plays an important part, as is evident from the fact that the detection efficiency decreases with rising ambient temperature. There is no appreciable difference in detection efficiency between the three diodes considered at temperatures up to 40 °C.

It should be noted that the germanium diode type OA 50 is adopted as an example to illustrate the effect of a high load-resistance. In other diodes, e.g. types OA 51, OA 61 and OA 71, the leakage is very much smaller, and the detection efficiency associated with a high load-resistance is therefore higher than in the above case.

Another point illustrated by fig. 6 which should be mentioned in passing, is that the diode part of the EAF 42 must not be operated with a low load-resistance; it is, in fact, designed to operate with a load of the order of 0.5 MΩ.

Equivalent attenuation resistance

An important factor in many circuits, apart from the detection efficiency, is the power extracted from the voltage source. In so far as the power absorbed depends on the detector circuit (it also depends, of course, on the magnitude of the signal voltage), it is usually defined in terms of the so-called equivalent attenuation resistance (R_d). This is the resistance which, if substituted for the detector circuit, would draw the same amount of power from the voltage source. If P be the power so extracted and E the peak voltage supplied by the particular source, the equivalent attenuation resistance R_d is defined by the equation:

$$\frac{E^2}{2R_d} = P. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Given a circuit as shown in fig. 4*a* with both the load-resistance (R) and the diode leakage-resistance ($R_{i\,\mathrm{inv}}$) high in relation to the diode forward resistance (R_i), the approximate value of R_d is readily evaluated. In this case (to be precise, when R and $R_{i\,\mathrm{inv}}$ are infinitely high), the D.C. voltage produced across the capacitor (V) is E (with $\eta_{\mathrm{det}} = 1$); the power dissipated in R is then E^2/R. Accordingly, a small current flows during the very short forward period (see fig. 4*b*); however, we shall ignore the power dissipated by this current in the forward resistance. The voltage across $R_{i\,\mathrm{inv}}$ is now, during virtually the whole period, given by $E\,(-1 + \cos\omega t)$, so that the power dissipated in $R_{i\,\mathrm{inv}}$ is $\frac{3}{2}\,E^2/R_{i\,\mathrm{inv}}$. Hence $P \approx E^2(1/R + 3/2\,R_{i\,\mathrm{inv}})$, and it follows, with the aid of (1), that:

$$1/R_d \approx 2/R + 3/R_{i\,\mathrm{inv}}. \quad . \quad . \quad . \quad (2)$$

Accordingly, the equivalent attenuation resistance of a vacuum diode ($R_{i\,\mathrm{inv}} = \infty$) is roughly equal to half the load-resistance, whereas in the case of a germanium diode ($R_{i\,\mathrm{inv}} \neq \infty$) the resistance R_d is equal to half the load-resistance and a third of the diode leakage-resistance in parallel.

Fig. 7 shows the calculated equivalent attenuation conductance G_d ($= 1/R_d$) versus the load conductance G ($= 1/R$), for different values of the leakage conductance $G_{i\,\mathrm{inv}}$ ($= 1/R_{i\,\mathrm{inv}}$), in the case of an idealized diode characteristic consisting of straight lines (constant forward and leakage resistances). The approximation involved in the above argument means that the tangents to the starting-points of the curves, seen at the bottom left-hand side of the diagram, are used instead of the curves themselves.

It is seen that the effect of increasing load and of increasing leakage upon the attenuation is not quite as serious as formula (2) suggests; however, this does not detract from the practical validity of this formula.

A difficulty in applying the formula arises from the fact that, as can be seen from the characteristics of the germanium diodes, the leakage resistance is governed by the voltage. Hence the average leakage-resistance appropriate to a given peak voltage must be estimated from the characteristic.

An increase in the signal voltage relative to zero will at first produce an increase in the average leakage resistance; but if the signal voltage increases

far enough, it will diminish again (fig. 3*b*). Accordingly, a high signal voltage and a high ambient temperature, both of which reduce the leakage resistance, impair the efficiency of a germanium diode.

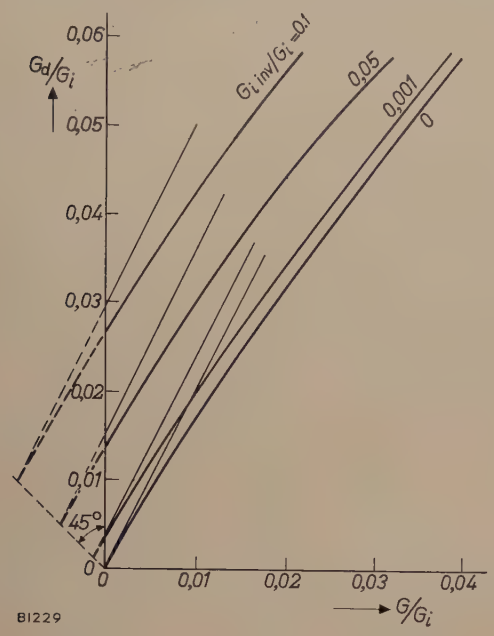


Fig. 7. Calculated attenuation conductance ($G_d = 1/R_d$) versus the load conductance ($G = 1/R$), for various values of the leakage conductance ($G_{i\,inv} = 1/R_{i\,inv}$), in the case of a diode with the characteristic shown in fig. 5*a*. As in fig. 5*b*, all the quantities involved are expressed in terms of G_i ($= 1/R_i$), that is, the forward conductance of the diode. To obtain the curve appropriate to a given value of $G_{i\,inv}/G_i$, transfer the $G_{i\,inv}/G_i = 0$ curve a distance equivalent to the particular value of $G_{i\,inv}/G_i$, first to the left, and then the same distance upwards.

From (2), if the load-resistance be reduced, the extra attenuation arising from leakage will become less important; in fact, given a sufficiently drastic reduction, it will be possible to substitute a germanium diode for a vacuum diode with virtually no change in attenuation. Practical experience has shown that the difference in attenuation becomes negligible at a load-resistance of some ten-thousands of ohms. Of course, the precise load-resistance to produce this effect depends upon $R_{i\,inv}$, which, in turn, depends upon the particular type of germanium diode, and upon the ambient temperature and the applied A.C. voltage. Now, given a load-resistance of the above-mentioned order of magnitude, the detection efficiency of the various types of germanium diode, and that of the vacuum diode type EB 91, will all be in the region of 100%; hence there will be virtually no difference in performance between any of them. However, any further reduction of R will affect both the attenuation and the detection efficiency unfavourably. Whereas the equivalent attenuation resistance of any diode will then remain equal to half the load-resistance, the higher forward resistance of the germanium diode, as we have already seen, will give it a detection efficiency superior to that of the vacuum diode.

The above argument only holds good for a vacuum diode whose forward resistance is not unduly high. Given a vacuum diode having a high forward resistance, e.g. the EAF 42, the situation will be more complex because, amongst other reasons, such a valve operates in a range perceptibly affected by deviations from formula (2) (see fig. 7, bearing in mind that G_i is now low).

Provided that the signal voltage is low ($< 0{\cdot}5\ V_{eff}$) and the ambient temperature is not unduly high, it is usually possible to procure a better detection efficiency and less attenuation with germanium diodes than with vacuum diodes. The reason for this is that, under these conditions, vacuum diodes operate in the starting-current region; here the detection efficiency and the equivalent attenuation resistance are both low, and the relation $R_d = \frac{1}{2}R$ no longer holds good in this region. However, the behaviour of vacuum diodes under these conditions will not be pursued here.

In the region between 0 and about 10 μV, there is no difference in slope between the forward and reverse characteristics of a germanium diode; which then behaves like an ordinary resistor, that is, without rectification.

That the germanium diode is particularly suitable for use in circuits where the load resistance is fairly low and the signal voltage and ambient temperature not unduly high can be deduced from the above argument. However, the other advantages of the germanium diode as mentioned on the opening page of this article frequently turn the scale in its favour even in cases where the electrical properties of this diode do not match those of the vacuum diode.

Performance at high frequencies

The efficiency of a germanium diode as a detector at high frequencies (> about 40 Mc/s) cannot be properly predicted from the static characteristic. We have already seen something of the nature of the effects ("hole storage") precluding such a prediction in the preceding article [1]).

We shall now illustrate, with the aid of one or two practical examples, how these effects modify the performance of a germanium diode in a practical circuit. The values referred to are the results of tests on a TV video detector circuit containing a 3.9 kΩ load-resistor shunted by a capacitor of roughly 20 pF. Given a germanium diode type OA 50, and a signal of r.m.s. voltage 5 V, the measured detection efficiency of this circuit is 0.62 at 30 Mc/s and 0.605 at 70 Mc/s.

The first thing that we notice about these values is that the detect efficiency is quite low at both frequencies. This is partly attributable to the fact that, particularly at 30 Mc/s, the time constant of the load is not very long compared to one cycle; it is also attributable to the self-capacitance of the diode, owing to which an appreciable part of the H.F. voltage occurs across the load (20 pF). The difference in the detection efficiency as between the two frequencies is only small but the difference in the attenuation caused by the detector circuit in the circuit immediately preceding it is considerable: the equivalent attenuation resistance is 2400 Ω at 30 Mc/s and 1450 Ω at 70 Mc/s. Since the D.C.voltage across the load-resistance and therefore the power dissipated in it is very much the same in both cases, the relatively greater attenuation at 70 Mc/s must be attributed to extra losses in the germanium diode. In a TV receiver, such strong attenuation detracts from the gain of the amplifier stage preceding the detector; moreover, owing to the variation in attenuation between individual diodes of the same type, it is responsible for variations in the amplification and in the frequency characteristic of production receivers.

It is also worth mentioning that the decline in performance at relatively high frequencies is all the more noticeable according as the load-resistance is increased.

Examples illustrating the use of diodes for special purposes

As we may conclude from the above, the germanium diode may be substituted for the vacuum diode in a very large number of cases. At the same time, the leakage exhibited by the germanium diode, must often be taken into account in the design of a particular circuit. With this reservation, however, there is freedom of choice from several types, according to the particular application envisaged; these include types of low leakage and high maximum reverse voltage (*fig. 8*).

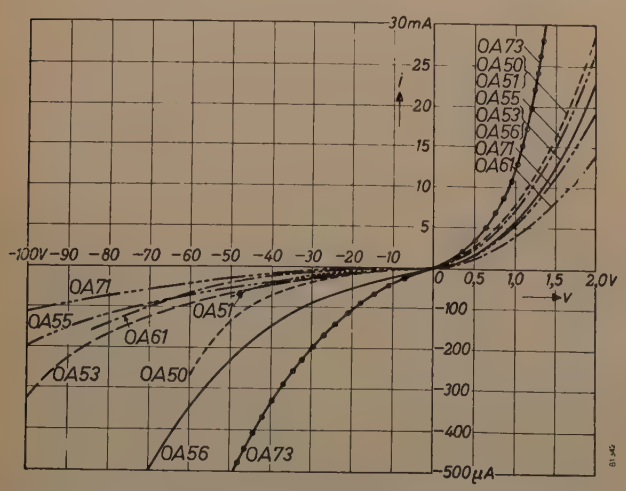


Fig. 8. The characteristics of various types of germanium diode.

Video detection

Fig. 9 is the circuit diagram of a video detector employing a germanium diode, i.e. type OA 60 or type OA 70. As we have already seen, these diodes are specially designed for use in such a circuit. In the case here considered, the operating frequency is 24 Mc/s and the signal voltage in the I.F. circuit (L_2-C_2) is 5 V r.m.s.; the detection efficiency is then about 70% that is, the D.C. voltage generated across the 3·9 kΩ load-resistor (R) is about 5 V. The equivalent resistance of the detector circuit is about 3 kΩ.

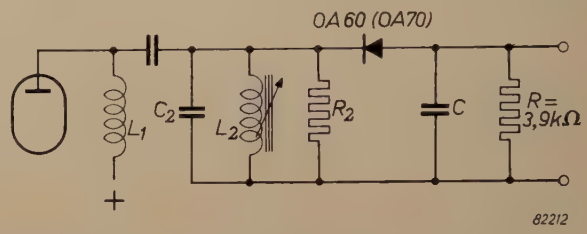


Fig. 9. Video circuit containing a germanium diode type OA 60 or OA 70.

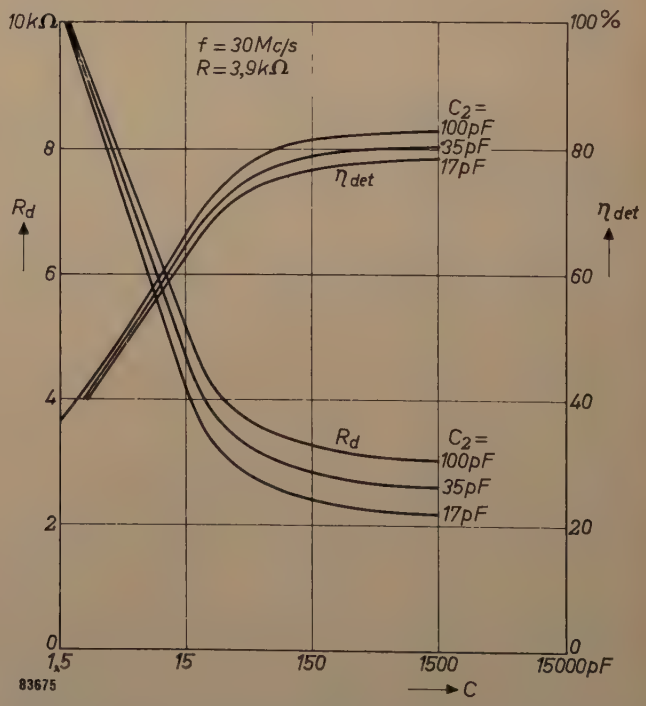


Fig. 10. Effect of the load-capacitance C on the detection efficiency η_{det} and equivalent attenuation resistance (R_d) of the video detector circuit shown in fig. 9. These quantities also depend upon the tuning capacitance C_2; the curves for several values of this parameter are given. The curves are valid for a carrier-wave frequency of 30 Mc/s and a load-resistance R of 3.9 kΩ.

The detection efficiency and the attenuation are also affected by the total tuning capacitance (C_2) of the circuit (see *fig. 10*), which, in the diagram shown in fig. 9, comprises the self-capacitance of the coils and the valve and wiring capacitances (totalling about 17 pF in all).

D.C. restoration

Fig. 11a shows a circuit employed to fix the black level in the signal applied to the picture tube of a television receiver. This circuit includes a germanium diode, type OA 61 or type OA 71, specially designed for the purpose and exhibiting only a small amount of leakage even when operated with a high reverse voltage.

exactly to any rapid variations in v_1 (potential at point 1).

However, as soon as v_2 drops below v_3, as it does during the application of a synchronizing pulse (fig. 11*c*), the diode becomes conductive. A charging current then flows to C so that, at the end of the sync. pulse, v_2 (which is also the control-grid potential of the picture tube W) is raised to the fixed value represented by v_3. Potential v_1 then increases again, thus initiating the next line period, during which v_2 again responds almost exactly to the variations of v_1. Owing to the fact that a small proportion of the charge of C leaks away through R_1 during the line period, voltage v_2 again drops below v_3 at the next sync pulse; however, this leakage is made good and a new line period starts from v_3 (fig. 11*c*). The necessity of ensuring that v_2 will drop below v_3 during each synchronising pulse imposes a maximum limit on the size of R_1.

The direct current flowing in potentiometer R causes v_3 to assume a certain value below the cathode potential; hence this potentiometer can be used to vary v_3 and so adjust the

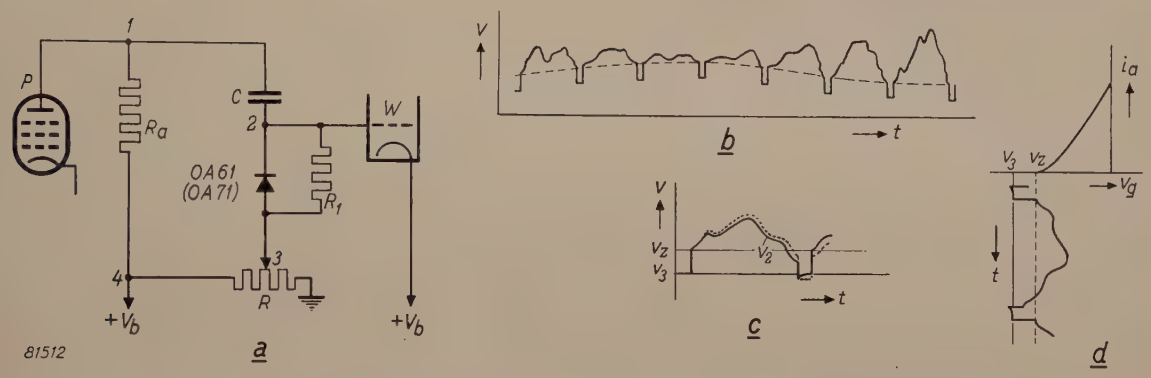


Fig. 11. *a*) D.C. restorer circuit employed to fix the black level of the signal applied to the picture tube W of a television receiver.
b) Video signal with line-synchronizing pulses, as applied to the grid of the picture tube when the diode shown in (*a*) is omitted. In practice, the variation of the sync. pulse peaks is much more gradual than this diagram suggests.
c) Video signal on the grid of the picture tube (full line). Each line-period starts at a fixed value (v_z) corresponding to the pre-adjusted black level of the picture tube. The dotted line represents the signal as it would be if not corrected by the diode and the resistor R_1.
d) The video signal referred to the i_a-v_g characteristic of the picture tube. With the aid of potentiometer R(see (*a*)), v_3 is so adjusted that v_z (the black level) coincides roughly with the cut-off point of the tube-characteristic.

The action of such a circuit will be explained here for those unfamiliar with TV circuit technique. Fig. 11*b* shows roughly what the shape of the video signal on the grid of the picture tube would be in the absence of a diode. The upper ends of the sync. pulses, which correspond to black in the scene televised, should remain at a constant level in order that black in the scene will always give rise to the same degree of blackness on the picture tube. However, it will be seen that these peaks rise and fall with the average picture-content of the video signal preceding them. Accordingly, the task of the circuit shown in fig. 11*a* is to fix the black level at the start of each line period, thus correcting any variation in this level introduced during the preceding line period, that is, preventing any *cumulative* variation. Because the depth of the synchronizing pulses is constant, it is sufficient to maintain the bases of these pulses at a fixed level. This is achieved as follows.

As long as the potential (v_2) of the bottom plate of capacitor C remains above the potential at point 3 (v_3), the diode remains non-conductive. Owing to the high resistance of R_1, the charge and potential difference of the capacitor C can vary only gradually; hence v_2 must respond almost

black level of the picture tube to a particular fixed value (fig. 11*d*).

If much of the charge of capacitor C leaks away through the diode in the interval between two successive sync. pulses, the grid voltage (v_2) of the picture tube (W) will already have fallen well below the pre-adjusted black level (v_z) by the time the second sync. pulse arrives (fig. 11*c*). One detrimental effect of this premature drop in v_z is that the side of the picture at which the raster-lines end becomes darker than the side where these lines start. There is, however, still another, more serious disadvantage. With such a drop, the diode becomes conductive, and therefore the charging of C commences before the sync. pulse is fully developed. Instead of flowing in R_a, as under ordinary conditions, the greater part of the anode current of valve P then

takes the line of least resistance through C, thus reducing the amplification of the valve abruptly and considerably. As long as the charging current continues to flow — that is, during a considerable part, if not the whole, of the pulse period (since the considerable amount of charge at first released must now be made good) — the pulse is unable to develop to its full height and is therefore distorted and attenuated. This effect may attain such proportions as to upset the synchronization of the picture.

This explains why it is necessary in this application to employ a diode exhibiting only a small leakage at the high reverse voltages involved.

Summary. Among the obvious advantages of germanium diodes compared with their vacuum equivalents, are their relatively small size and weight and the fact that they contain no filament. As regards the normal functions of a diode, that is, rectification and detection, the leakage current of the germanium diode and its superior forward characteristic, constitute the most striking differences between it and the vacuum diode. The effect of these differences upon the detection efficiency and equivalent attenuation resistance in a detector circuit is investigated. It is shown that germanium diodes can be employed in a very large number of cases and that, provided that the load-resistance is low and the signal voltage and ambient temperature are not unduly high, the performance of such a diode is even better than that of a vacuum diode. Special germanium diodes have been developed for certain purposes, e.g. to operate at high frequencies (video detection in a television receiver) and for use as D.C. restorers for maintaining the black level in the picture tube of a TV receiver.

SEDIMENTATION OF FLUORESCENT SCREENS IN CATHODE RAY TUBES

by F. de BOER and H. EMMENS. 535.371.07:621.385.832

The ever-increasing use of cathode ray tubes for television and other purposes creates the need for a sufficiently reproducible method of forming the fluorescent screen in the tube. The problems thereby involved are largely of a colloid-chemical nature. A detailed study of the effects occurring on sedimentation of the screen is possible only if the chemical composition of the layer is known. This composition can be determined with the aid of radio-active tracers.

Introduction

The fluorescent screens of picture-tubes and other types of cathode ray tube are composed of a mixture of substances. The fluorescent substance itself, the so-called phosphor, of course predominates, but for the deposition of the screen it is necessary to include a number of components to ensure a sufficiently adhesive and finely grained layer. These admixtures affect the characteristics of the screen, such as the secondary emission factor. If this is too low, heavy negative charging of the (insulated) screen will occur during use, to the detriment of the luminous efficiency and fidelity of reproduction [1]). On the other hand, the content of non-fluorescent substances must not be too high, as this also has an unfavourable effect on the fluorescent efficiency. It is therefore necessary to select and apportion the additional constituents with care.

The method of preparation of fluorescent mixtures nowadays employed is as follows. The fluorescent grains are suspended in water containing waterglass (a colloidal solution of potassium silicate in water with excess silica). A gelatinising agent is also added. This suspension is poured into the tube and, after a certain time, the powder settles to form a uniform, closely adhering layer, the solvent being then poured off. *Fig. 1* shows how this is done in manufacture.

The use of a gelatinising agent is necessary to prevent the layer of sediment from sliding to one side and also to prevent individual granules from becoming detached, when the tube is tilted in the decanting process. Moreover, in the dry condition, during exhaustion of the tube as well as during use, effective adhesion of the granules must be guaranteed; the presence of loose granules in a tube operated at high voltages must be avoided at all costs.

Until a few years ago the gelatinising medium used was potassium sulphate, but a disadvantage of this "sulphate" method is that it takes some time to produce a sufficiently adhesive layer, viz. 1 to 2 hours. A more rapidly reacting medium was therefore sought. Such a medium was found among certain soluble calcium or barium salts, of which barium nitrate, for example, produces a firmly

[1]) See for example J. de Gier, A. C. Kleisma and J. Peper, Secondary emission from the screen of a picture tube, Philips tech. Rev. **16**, 26-32, 1954/55.

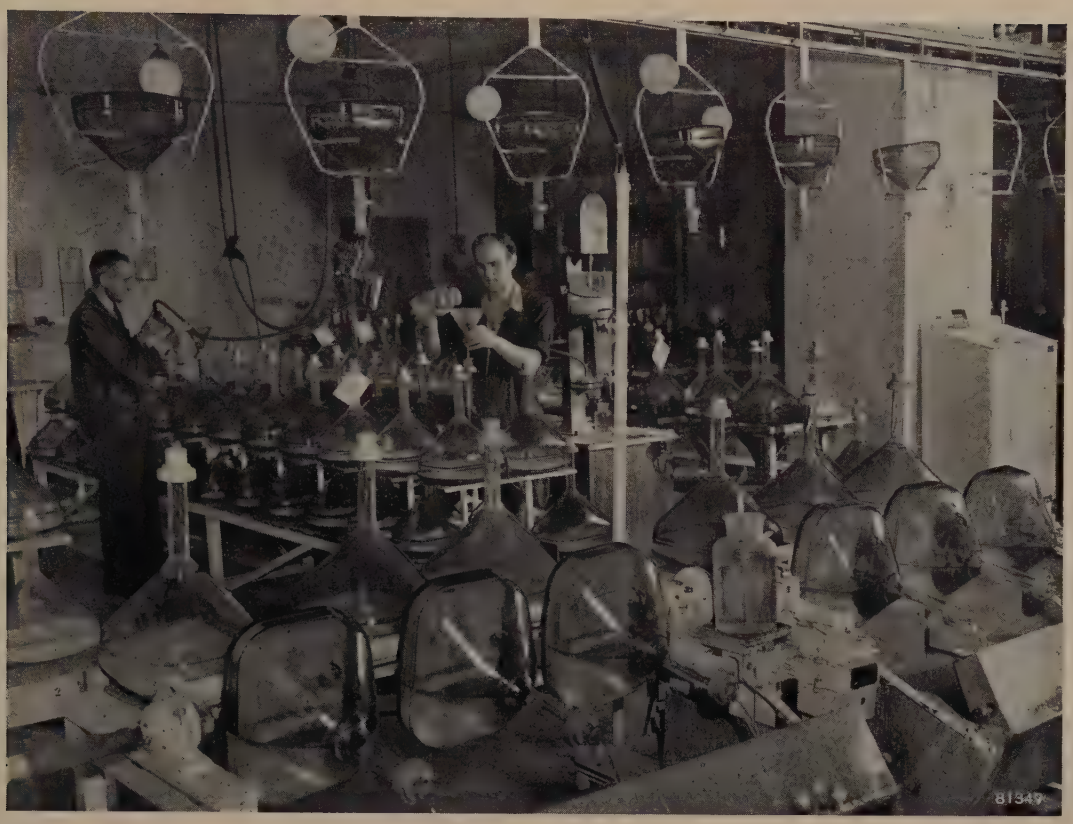


Fig. 1. Photograph of the manufacturing process for the application of the screens to television picture tubes. The tubes enter the settling room on an overhead conveyor. Background: filling with the liquid containing the phosphor and binding agents in suspension. Foreground: decanting the liquid.

attached layer in roughly 15 minutes. This represents a considerable advantage in mass production, but the use of barium salts for this purpose nevertheless has the disadvantage that the secondary emission factor of the deposited screen is lower than that of screens made by the sulphate method. Particularly in modern tubes, operated with very high acceleration potentials — at which the secondary emission is in any case fairly low — this is an important consideration.

It will be obvious that the adhesive properties of the settled screen depend upon the composition of the solution. Screens prepared in accordance with the barium method yield the curve depicted in *fig. 2*. The various concentrations must be selected within the area to the right of the curve *BAC* in order to ensure a sufficiently adhesive layer. We shall refer to this diagram again later.

In order further to clarify the processes that take place while the layer is being formed, and to observe the relationship between the composition of the fluorescent screen and the secondary emission factor an investigation has been made into the potassium, barium and also the SiO_2 content of fluorescent screens prepared by the two different methods. This investigation, in which use was made of radio isotopes, will now be described briefly. First, however, it is worth considering the picture that has been built up of the actual mechanism of formation of the layer.

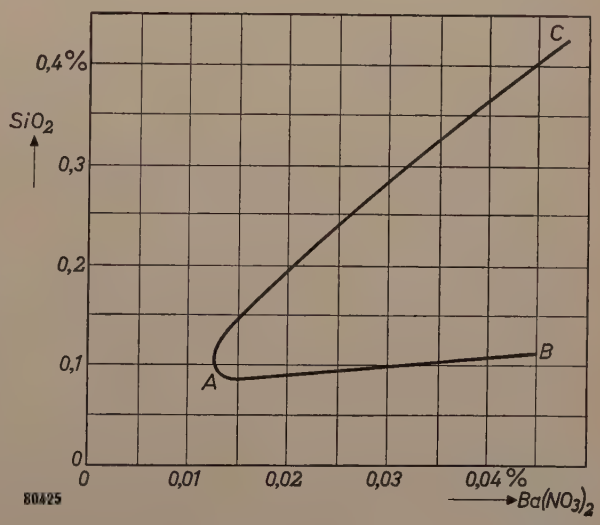


Fig. 2. Curve defining the conditions for adhesion of the fluorescent screen of a cathode ray tube. Vertical axis: concentration (% by wt) of waterglass, i.e. SiO_2, in the sedimentation liquid; horizontal axis: concentration of gelatinising medium (barium nitrate). In the area enclosed within the curve *BAC* effective adhesion of the screen is obtained.

Mechanism of formation of the layer

In the suspension, the granules of the fluorescent powder are coated with a slowly forming layer of silicate, and during sedimentation these layers come into contact with each other and coalesce into a gel, resulting in considerable mutual adhesion between the granules, and between them and the glass tube. In the absence of a gelatinising agent, hardly any gelling can take place, the adhesion is inadequate and the ultimate layer unstable.

Potassium sulphate owes its gelatinising properties solely to the electrostatic effect of the potassium ions, which partially neutralises the mutual electrostatic repulsion of the silica acid groups and thus promotes gelation. The potassium ions do not themselves function as constructional elements in the resultant gel and are therefore capable, in principle, of securing the adhesion of a practically unlimited number of granules. However, the gelatinising process takes a relatively long time for its completion (viz 1 to 2 hours, dependent on the potassium content) and hence much longer than the actual sedimentation.

Under otherwise similar conditions (equal acidity) barium salts produce much more rapid gelatinisation. (in about 20 minutes), but in the resultant gel the barium ions probably occur in the form of a compound. Once the gelatinisation is completed, no more barium ions will be available in the suspension, and granules which have by then not become attached to each other will not do so with the passage of time. The size of the granules in layers settled by the barium method are therefore, for a given barium concentration, limited.

Even without any fluorescent powder at all the presence of barium salts in the potassium silicate results in a gel, as seen by increasing turbidity of the liquid.

Determination of the composition of the layer

The composition of screens produced by the sulphate method can be easily determined by drying the settled layer after decanting the liquor, and leaching with distilled water. The phosphor granules do not dissolve, but the Si_2O-K_2O compound binding them together (briefly called binders in the following) do, and the solution can be analysed.

In the case of screens made with barium nitrate, however, such chemical analysis does not yield the desired results. Barium and potassium (from the water glass) are then both present and it is not a simple matter to separate the very small quantities concerned. A solution to this difficulty has been found in the use of radioactive tracers, viz. Ba^{133} (an artificial barium isotope of atomic weight 133), and K^{42} (potassium isotope, atomic weight 42). Both isotopes were prepared in the cyclotron at Amsterdam [2]). Ba^{133} has a half-life of 38.8 hours and it emits both soft γ radiation, with an energy of 0.3 MeV, and β radiation (conversion electrons). Neither radiation is very dangerous provided that the necessary precautions are taken in effecting the analysis. The half-life of K^{42} is shorter than that of Ba^{133}, viz. 12.4 hours, and the radiation emitted (γ) is harder and less innocuous; the energy is 1.5 MeV. As the time elapsing between preparation of the isotopes and their arrival at Eindhoven was about 16 hours, i.e. of the same order as the half-lives just mentioned, it was necessary to carry out the investigation immediately on receipt of the isotopes.

The barium in the form of the nitrate was received in bottles, packed in lead and consisting of a solution of 100 mg nitrate in 100 cc water. Immediately on receipt the solution was diluted with 500 cc distilled water, the necessary precautions being observed. Owing to absorption of the electrons in the water the isotope was thus rendered safe enough to carry out the various operations by hand, provided that this was done reasonably quickly.

The radioactive potassium arrived as an aqueous solution of KCl and was similarly diluted. This solution could also be handled quite safely in the ordinary way for a short period of time.

To a known quantity of the solution to be used for the screens, and containing the normal barium nitrate, 50 cc of the radioactive solution was added. Because of the chemical identity of all barium atoms, regardless of their weight, a homogeneous mixture of radioactive and non-radioactive barium results: hence the radioactivity of a portion of the mixture is a measure of the total quantity of barium in that portion. After sedimentation the liquid was decanted from the tubes by mechanical means. In this way 99 % of the radioactive substances was disposed of down the sink where, owing to the degree of dilution and the short half-life, they could do no harm locally. The residual radiations within the tube were also harmless. When dried, the deposited fluorescent powder was scraped off and spread out on an aluminium dish and the barium content was ascertained by measurement of the radiation intensity with a Geiger counter. For control purposes, a count was first taken from a preparation containing the same quantity of

[2]) A. H. W. Aten, and J. Halberstadt. The production of radio-isotopes, Philips tech. Rev. **16**, 1-12, 1954/55.

fluorescent powder and a *known* quantity of Ba^{133} of the same age as that used in the analysis.

To determine the quantity of potassium in the deposited layer, a similar procedure was followed, except that in this case 50 cc of the radioactive potassium solution was initially added to the normal barium nitrate solution.

The necessary correction was of course made for the background counts (cosmic radiation, etc).

The SiO_2 content of the powder was determined by normal chemical methods.

Results of the investigation

The table below gives some of the results relating to the proportions of BaO and SiO_2 in the binder as a function of the concentration of barium nitrate and potassium silicate in the liquid. From this it is seen that the molecular ratio BaO-SiO_2 in the binder is practically independent of the composition of the liquid, which agrees with the view expressed above that we are not here concerned with an evaporated solution yielding a mixture, but that the barium and SiO_2, are present in the binder in the form of a sort of compound. Another argument in favour of this conclusion is that the quantity of binder is roughly proportional to the Ba content of the solution. On the other hand, a very strong binding, of the nature of an adsorption, could explain these facts.

In *fig. 3* the K_2O-SiO_2 ratio in the binder is shown plotted against the concentration of potassium silicate in the solution. Curve *1* refers to screens made by the sulphate method, and curve *2* to the barium nitrate method. Clearly there is no question of the K_2O-SiO_2 ratio in the binder being constant.

These conclusions are fully in accordance with what has been said above regarding the behaviour of the gelatinising media in the solution. The diagram in fig. 2, representing the conditions for good adhesion of the settled screen can now be explained as follows. The line *AB* represents the (linear) relationship between the quantity of binder deposited and the barium concentration of the solution. To the left of *A*, the barium concentration is too low to produce a sufficiently adhesive layer, whilst below the line *AB* the SiO_2 content is too low. The time needed to ensure a properly adhesive layer increases with the

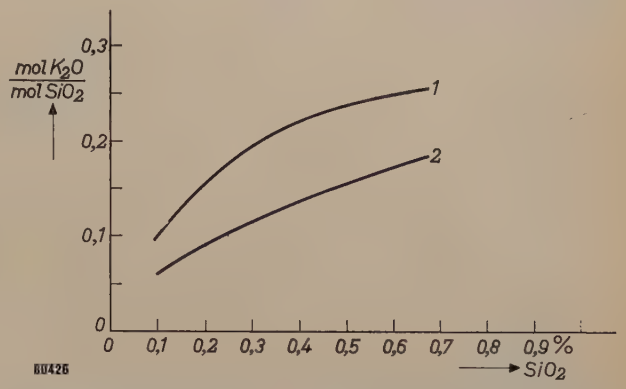


Fig. 3. Relationship between the molecular ratio K_2O-SiO_2 in the binder, and the silicate concentration (% by weight) in the solution. *1*) screens made by the sulphate method, *2*) screen made by the barium method.

concentration of potassium (derived from the waterglass), and, above the line AC this time is so long that the layer is no longer stable. The slope of the curve *AC* implies that adhesion is improved as the barium content of the solution is increased.

Some idea of the thickness of the adsorbed layer of binder around the phosphor granules can be obtained from the relationship between the absolute quantity of binder settled and the phosphor concentration of the suspension. This is shown in *fig. 4*; the relationship is practically linear. The intersection

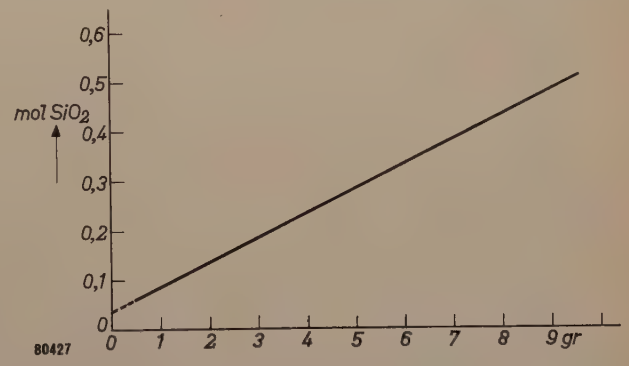


Fig. 4. Quantity of deposited binder plotted against quantity of phosphor in the suspension. The intersection of the curve on the vertical axis represents the quantity of binder deposited on the glass. The slope is a measure of the quantity of binder adsorbed per granule of phosphor.

Table. Analysis of the molecular ratio BaO-SiO_2 in sedimented layers.

Percentage by weight $Ba(NO_3)_2$ in the liquid	Percentage by weight SiO_2 in the liquid	Molec. ratio BaO-SiO_2 in liquid	Molec. ratio BaO-SiO_2 in binder	Quantity of binder deposited		
				BaO	SiO_2	Total
0.02 %	0.25 %	1:32	1:16	1.5 mg	9.4 mg	10.9 mg
0.02	0.38	1:48	1:18	1.2	8.6	9.8
0.02	0.53	1:64	1:16	1.3	8.0	9.3
0.01	0.12	1:32	1:19	0.7	4.8	5.5
0.01	0.19	1:48	1:19	0.7	4.8	5.5
0.01	0.26	1:64	1:22	0.7	5.9	6.6

of the curve on the vertical axis is a measure of the quantity of binder deposited on the glass screen. If the grain size of the phosphor be known it is possible to calculate from the slope of the line the quantity of binder per granule and, from this, the thickness of the adsorbed layer. A thickness of the order of 100 Å (10^{-6} cm) was found, and this agrees with the results of tests to ascertain the acceleration voltage that has to be applied to the tube to produce perceptible fluorescence. The acceleration voltage determines the depth of penetration of the electrons into the layer of binder. It is found that the penetration depth appropriate to the observed minimum acceleration voltage is also of the order of 100 Å.

It is important, especially for high-voltage cathode-ray tubes, that the potassium concentration in the screen should be as high as possible since, as explained above and as shown in *fig. 5*, this is accompanied by a high secondary emission factor of the screen. As indicated by the results plotted in fig. 3 this can be ensured by making the concentration of potassium silicate in the liquid as high as possible. This does not alter the BaO-SiO_2 ratio of the screen, but the time taken to secure satisfactory adhesion, is increased.

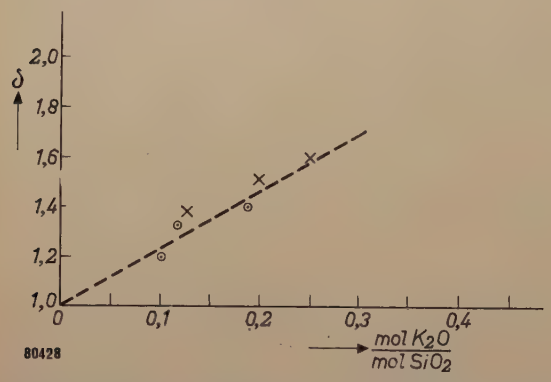
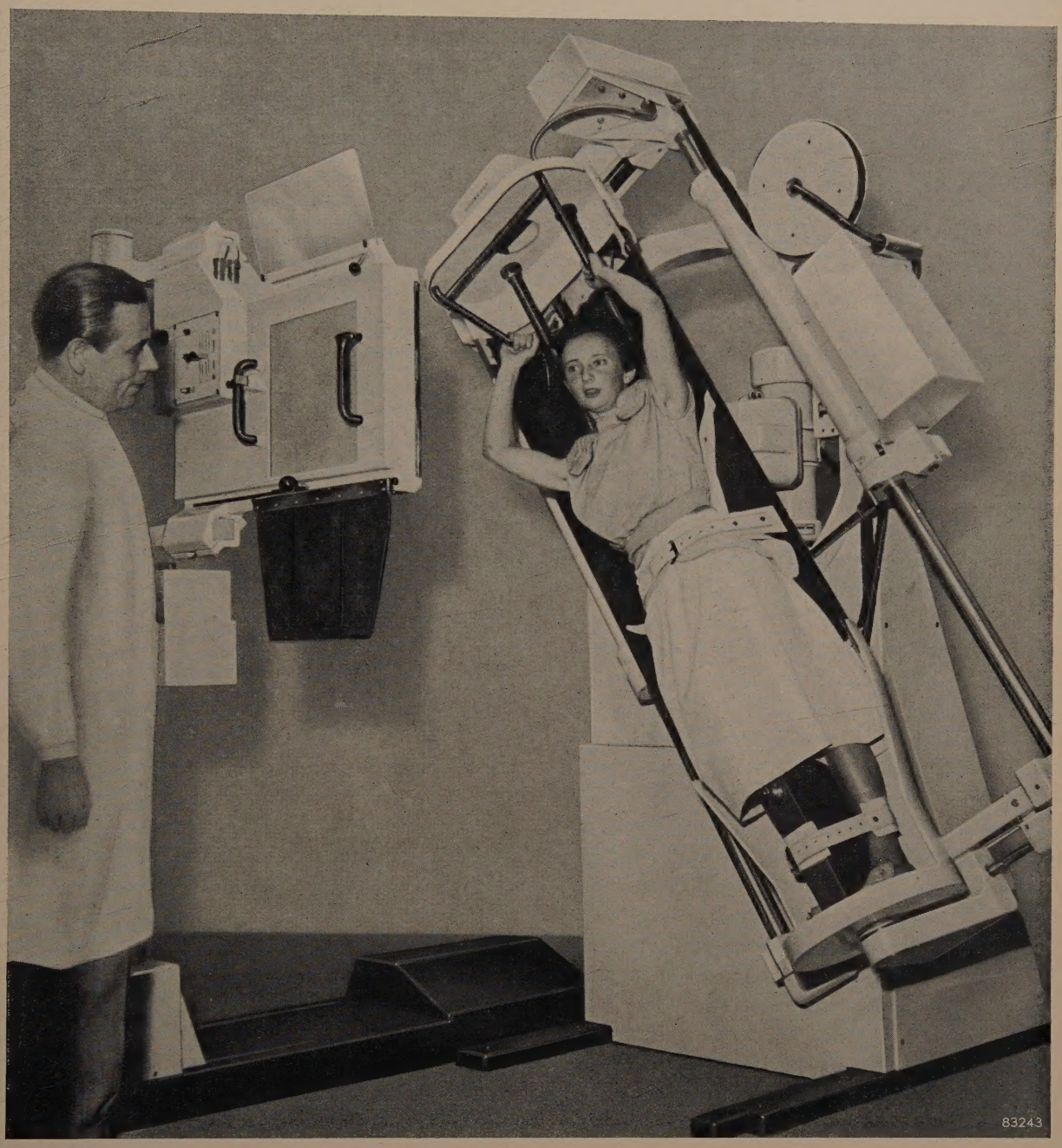


Fig. 5. Secondary emission factor δ of the fluorescent screen plotted against the molecular ratio K_2O-SiO_2 in the binder. The points denoted by crosses relate to screens prepared by the sulphate method; those shown as circles relate to the barium method.

As will be seen from fig. 3, the highest potassium concentration in the screen is obtained by employing the sulphate method; this concentration is of course reduced if part of the potassium be replaced by barium. On the other hand, as already pointed out, the addition of barium promotes rapid adhesion, so that it is necessary to aim at a composition for the suspension that will include enough barium to ensure reasonably rapid adhesion, but not so much that the secondary emission factor of the screen is reduced beyond the permissible limit.

Summary. The fluorescent screen in TV and other types of cathode ray tube is produced by sedimentation from a suspension. This article deals with the processes that take place during this desimentation. The effect of gelatisining agents on the adhesive properties of the screen is found to be very pronounced. Until recently potassium sulphate was used as gelatinising agent, but at the present time preference is given to barium salts, which promote more rapid adhesion. The chemical analysis of screens made from various solutions leads to some understanding of the behaviour of the gelatinising agents. For the analysis of the Ba and K in screens settled with barium salts, use was made of tracers, i.e. radio-isotopes of these elements, which also made possible an investigation into the effect of the composition on the secondary emission factor of the screen.

"MÜLLER" UGX APPARATUS FOR X-RAY DIAGNOSTICS



Apart from the X-ray tube and generator and the equipment for observing the X-ray picture, a diagnostic apparatus must also be provided with mechanical means for placing the patient in any position necessary for the examination. The usual type of universal diagnostic apparatus provides for the tilting of the patient about a horizontal axis perpendicular to the X-ray beam, and the X-ray tube and fluorescent screen or camera must follow this movement.

With the new apparatus shown, this conventional arrangement has been abandoned in favour of a fixed X-ray source and screen. (The protective screening is then also fixed and the radiologist does not need to move in order to continuously observe the X-ray picture). Instead of tilting the patient about the above-mentioned axis, this apparatus can turn the patient about a horizontal axis parallel to the direction of the X-ray beam and about his longitudinal axis. In this way, quite new positions of the patient and new irradiation directions are possible, which may be of great value for the examination of certain organs.

The apparatus, which has been developed by H. Verse and K. Weigel of Hamburg, was first demonstrated at the 7th International Congress of Radiology [1]) in Copenhagen, 1953. The apparatus will be more fully described in this Review in due course.

---

[1]) H. Verse and K. Weigel, Ein gerätetechnische Betrachtung zur Röntgendiagnostik, Fortschr. Röntgenstrahlen **80**, 520-524, 1954, No. 4.

ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN

Reprints of these papers not marked with an asterisk * can be obtained free of charge upon application to the Philips Electrical Ltd., Century House, Shaftesbury Avenue, London W.C. 2.

2105*: J. C. Francken: Electron optics of the image iconoscope (Thesis, Delft, 1953).

Chapter I deals with the so-called cathode lens, an electrostatic lens which differs from ordinary immersion systems in that the electrons leave the object with nearly zero velocity. The image iconoscope, in which the image is formed by a cathode lens placed in a rotationally symmetric magnetic field, is then briefly discussed. In Ch. II the electrostatic field is discussed. General solutions of the rotationally symmetric Laplace equation are applied to a case which resembles that of the image iconoscope. For measurement of the field a resistance network was used. This method is analyzed and improved. In Ch. III the magnetic field of the deflection coil is dealt with. The measuring method of Van Mentz and Le Poole was used, and is examined as to accuracy. In Ch. IV the general and the paraxial equations for the trajectories are given, and the conditions specified under which the latter may be used. In Ch. V solutions of these equations in the form of expansions are found which lead to a general solution for the electron trajectories in the type of electron lens considered. In Ch. VI the paraxial trajectories in the Philips image iconoscope 5840/00 are calculated. A comparison is made between tubes with and without an "anode mesh". The computing methods used are discussed at some length and examined as to their accuracy. The mechanism of the image formation is explained with the aid of the computed electron trajectories. The definition of cardinal points is adapted to the special character of this type of electron lens. In Ch. VII experiments are described which provide a relation between the shape of the imaging coil and the magnification and rotation of the image. These experiments lead to a type of coil which permits a continuously variable magnification without rotation of the image. Ch. VIII and IX deal with aberrations, ion spot and diamond distortion. Finally, in Ch. X, the application of variable magnification in television cameras is discussed (see also Philips tech. Rev. **14**, 327-335, 1952/53).

2106: J. F. van Wieringen: Influence du traitement mécanique sur la résonance paramagnétique du manganèse dans les poudres de sulfure de zinc (Physica **19**, 397-400, 1953). (Influence of mechanical treatment on the paramagnetic resonance of manganese in zinc sulphide powders: in French)

If wurtzite, the hexagonal modification of ZnS, is compressed at room temperature, it changes into sphalerite, the cubic modification. This has been observed by X-ray diffraction. The gradual transition manifests itself also in the paramagnetic resonance spectrum of small quantities of Mn dissolved in ZnS. This is because the paramagnetic resonance spectrum of divalent manganese is very sensitive to the presence or absence of non-cubic components of the surrounding crystalline field. The spectrum as a function of Mn concentration is shown. In non-compressed wurtzite powders the complete spectrum is resolved at higher concentrations (0.05%) than had been reported before (0.001%) for compressed powders.

2107: K. F. Niessen: Condition for vanishing spontaneous magnetization below the Curie temperature (Physica **19**, 445-450, 1953).

For a special spinel structure in which the spontaneous magnetization at a temperature T_0 below the Curie temperature (T_c) becomes zero, a method has been derived to determine the temperature T_0. A condition is derived for the extreme case $T_0 = T_c$ which can be applied to experiments for finding the ratio of mutual interactions of magnetic ions.

2108: H. G. van Bueren: A model for demonstrating dislocations in crystals (Brit. J. appl. Phys. **4**, 144-145, 1953).

A simple dynamic model, in which the interatomic forces are simulated partially by magnetic forces and partially by the elastic forces exerted by small springs, is described. With it the movement of edge and screw dislocations through a crystal lattice can easily be demonstrated.

2109: D. Polder and J. Smit: Resonance phenomena in ferrites (Rev. mod. Phys. **25**, 89-90, 1953).

With the help of a model, consisting of an ellipsoid of ferrite with Bloch-walls perpendicular to one of the major axes, it has been demonstrated that considerable resonance losses can occur in ferrite throughout a very wide frequency band, viz. from the natural resonance frequency predicted by Snoek

up to the frequency of the Larmor-precession in a magnetic field of intensity of $4\pi M_s$, where M_s represents the saturation moment of the ferrite.

2110: H. P. J. Wijn, M. Gevers and C. M. van der Burgt: Note on the high frequency dispersion in nickel zinc ferrites (Rev. mod. Phys. **25**, 91-92, 1953)

In connection with a publication by Rado and others regarding two dispersion regions in ferrites, the behaviour of the imaginary component μ'' of the initial permeability ($\mu_i = \mu' - j\mu''$) is investigated in the frequency range 3Mc/s — 3000 Mc/s, in nickel-zinc ferrites of various compositions (18-50% NiO, 32-0% ZnO). No more than one resonance maximum is found. It is concluded from the behaviour of μ_i as a function of the frequency during tensile stresses (up to 2.7 kg/mm^2), that the dispersion in these ferrites is linked up with a rotation process of the spin vectors.

2111: H. P. J. Wijn and H. van der Heide: A Richter type after-effect in ferrites containing ferrous and ferric ions (Rev. mod. Phys. **25**, 98-99, 1953)

With manganese-zinc ferrite (28 MnO, 19 ZnO, 3 FeO, 50 Fe_2O_3) for each frequency f, the value of tan δ as a function of the temperature T shows a maximum at a temperature T_{max}. The relationship between $1/T_{max}$ and f is linear, which suggest an activation energy (0.11 eV). This effect is not found when a nickel-zinc ferrite is sintered at 1250 °C, but it is present when the sintering process takes place at 1525 °C, when 0.5% of Fe^{2+} ions are formed. Here too, the activation energy is approx. 0.1 eV. This leads to the conclusion that the residual losses in ferrites containing both ferrous and ferric ions are due to electron diffusion.

2112: G. W. Rathenau: Saturation and magnetization of hexagonal iron oxide compounds (Rev. mod. Phys. **25**, 297-301, 1953)

Review of results formerly published elsewhere (see Philips tech. Rev. **14**, 1952/53 and these Abstracts No. 2059). The value of the saturation magnetization at absolute zero of $BaO.6Fe_2O_3$ and related compounds can be explained as due to non-compensated anti-ferromagnetism. The Bloch wall formation in small particles is discussed. One is led to the assumption that in these materials Bloch walls are nucleated at imperfections. In specimens containing randomly oriented large crystals, Bloch wall formation becomes appreciable at a positive field strength of the order $4\pi I_s$. By orienting the crystals in a magnetic field $(BH)_{max}$ values of 3×10^6 gauss oersted have been obtained. The critical diameter for wall formation changes with temperature. An excess of walls formed at a different temperature from the temperature of measurement may persist in a metastable equilibrium.

2113: E. W. Gorter and J. A. Schulkes: Reversal of spontaneous magnetization as a function of temperature in Li-Fe-Cr spinels (Phys. Rev. **90**, 487-488, 1953)

Néel's theory of non-compensated anti-ferromagnetism predicts that in some materials the spontaneous magnetization should change its sign below the Curie temperature, since it is the difference between the anti-parallel magnetizations of the two sublattices, each of which may vary differently with temperature. This behaviour has been established for a series of Li-Fe-Cr spinels.

2114: J. S. van Wieringen: Anomalous behaviour of the g-factor of Li-Fe-Cr-spinels as a function of temperature (Phys. Rev. **90**, 488, 1953)

The g-factor of the spinel mentioned in abstract No. 2113, which has the value 2 at 0°K, rapidly decreases above 200°K. Starting from high temperatures (450°K), at which g is likewise about 2, g increases as the temperature is reduced and approaches infinity at $T = 337$°K. A qualitative explanation of this behaviour is derived from Kittel's g-formula and from the change of the spontaneous magnetisation as a function of temperature.

2115: J. M. Stevels: Le verre considéré comme polymère (Verres er Réfractaires **7**, 91-104, 1953)

Certain properties of silicate-glasses do not depend on the kind of network-modifying ions, but mainly on the number of bridging oxygen ions per tetrahedron, Y, a number which also indicates the number of contact points of each tetrahedron: Y, therefore, is a measure of the internal coherence of the network. The physical properties of the glass are very considerably influenced by this internal coherence of its network: glasses whose Y-value lies between 4 and 3 are machnically strong and chemically resistant; at values between 3 and 2 the glass becomes less and less resistant; if $Y = 2$ chains of unlimited length occur, held together by the network-modifying ions, thus constituting an extremely weak lattice, highly susceptible to thermal and mechanical influences. If Y is smaller than 2,

the length of the chains is no longer unlimited; silicates whose chains possess a high degree of symmetry may crystallize in spite of their great length. The phosphates, on the other hand, having a non-symmetrical structure, may still yield vitreous substances at Y-numbers as low as 1.6. As regards silicates, however, a small disturbance of the symmetry may suffice to prevent crystallisation: similar situations are frequently met in the chemistry of organic polymers. These considerations are confirmed by the examination of the dielectric losses of the glass in a H.F.electric field. At very low temperatures "deformation losses" of the network are found to occur, due to the sudden transition into another position of certain portions of the network chains. As the Y-value of the glass decreases, the deformation losses as a rule become greater, whilst the maximum of these losses as a function of the temperature is shifted to increasingly high temperatures.

2116: W. J. Oosterkamp: General considerations regarding the dosimetry of roentgen and gamma radiation (Appl. sci. Res. **B3**, 100-118, 1953 and addendum Appl. Sci Res. **B3**, 477 1954).

A distinction is made between the quantities "dose" (ionising ability, measured in roentgen), and "absorbed dose" (energy imparted by the radiation measured in rads or ergs per gramme). The methods by which both quantities can be measured are analysed. The measurement of dose at photon energies above 3 MeV has not yet been realised. The correlation between dose and absorbed dose is discussed. In air-equivalent or nearly air-equivalent material at moderate photon energies, dose is a fair measure of absorbed dose; in non air-equivalent tissue, the differences in mass absorption coefficient between this tissue and air should be taken into account; at discontinuities in the atomic composition, the increased generation of secondary electrons in materials with higher atomic number will also cause an increased ionization in neighbouring tissues with lower atomic number; at photon energies above 1 MeV there is an increasing discrepancy between dose and absorbed dose at the same place. (In the first-mentioned paper the author used the terms "irradiation" instead of "dose", and "dose" in place of "absorbed dose". The terms used in the second-mentioned paper and in this abstract are those since adopted by the International Commission on Radiological Units.)

2117: B. D. H. Tellegen: Synthesis of $2n$-poles by networks containing the minimum number of elements (J. Math. Phys. **32**, 1-18, 1953)

Brune's method for the synthesis of two-poles is extended to the synthesis of $2n$-poles. This leads to networks with the minimum number of reactances and the minimum number of elements.

2118: J. I. de Jong and J. de Jonge: Kinetics of the hydroxymethylation of phenols in dilute aqueous solution (Rec. Trav. chim. Pays-Bas **72**, 497-509, 1953)

The hydroxymethylation of phenols has been investigated in the pH range 1-11 and between 70-130°C in dilute aqueous solution. The reaction appears to be bimolecular. Below about pH = 4 the rates were found to be proportional to the concentration of the hydrogen ions, while a proportionality to the concentration of the hydroxyl ions was observed in more alkaline solutions. An influence of the concentration of buffers on the rates has not been observed. The presence of small amounts of triethanolamine does not influence the rate of the reaction. The mechanism of the reaction is discussed.

2119: J. D. Fast: Low-hydrogen welding rods (Welding J. **32**, 516-520, 1953).

See Philips tech. Rev. **14**, 96-101, 1952/53.

2120: J. I. de Jong: A determination of methylol groups in condensates of urea and formaldehyde (Rec. Trav. chim. Pays-Bas **72**, 652-654, 1953)

Methylol groups in condensates of urea and formaldehyde may be determined using an alkaline solution of potassium cyanide. Excess cyanide is back titrated with mercuric nitrate.

2121: N. W. H. Addink: Quantitative spectrochemical analysis by means of the constant-temperature D.C. carbon arc (Spectrochim. Acta **5**, 495-499, 1953)

Survey of the method developed by the author, of using complete evaporation in the D.C. carbon arc and projection of the spectrum on a standard paper density scale (s.p.d. scale). Some results are compared with those of conventional chemical analysis. See also Philips tech. Rev. **12**, 337-348, 1950/51.